Supporting information for

Trisulfur Radical Anion ($S_3^{\bullet-}$) Involved [1+2+2] and [1+3+1] Cycloaddition with Aromatic Alkynes: Synthesis of Tetraphenylthiophene and 2-Benzylidenetetrahydrothiophene Derivatives

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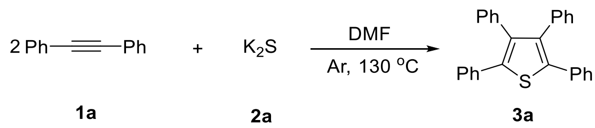
1. General Information

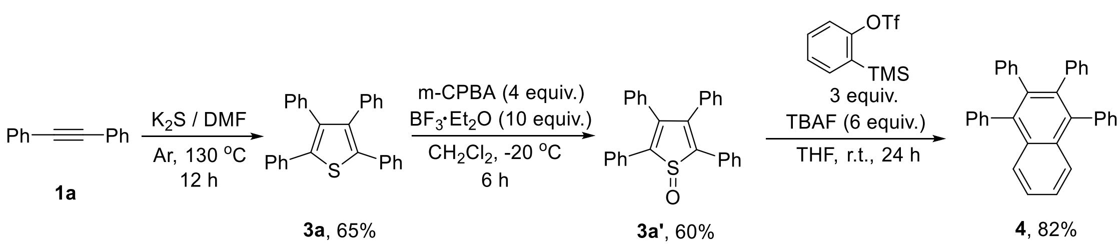
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 300-400 mesh silica gel was used. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 400 MHz spectrometer in $CDCl_3$ or DMSO-*d₆*. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) or DMSO-d_6 residual peak (δ 2.50) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16) or DMSO-d_6 (δ 39.52). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Melting points were measured on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER MICROTOF-Q III instrument with EI source. ESR spectra were detected by JES-X320 electron spin-resonance instrument.

2. Synthesis of tetraphenylthiophene 3a



A mixture of 1,2-diphenylethyne **1a** (0.60 mmol) and K_2S **2a** (0.60 mmol) in 2.5 mL dry DMF was stirred under an Ar atmosphere at 130 ℃ for 12 h. After completion of the reaction, as indicated by TLC, water (10 mL) was added, and the solution was extracted with ethyl acetate (3 × 15 mL). The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography using n-hexane on silica gel to afford **3a** in 69% yield. All remaining Polyaryl-substituted thiophenes (except **3j'**, **3k**, **3l**) were prepared using a procedure similar to that used to synthesize **3a**. The **3j'** was purified by flash column chromatography (hexane/EtOAc = 4:1) and The **3k** and **3l** were purified by flash column chromatography (CH_2Cl_2/CH_3OH = 15:1) to afford pure product.

3. Synthesis of 1,2,3,4-Tetraphenylnaphthalene 4

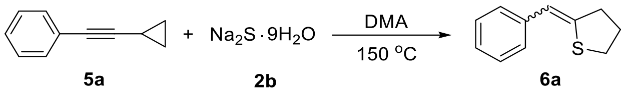


A 50-mL two-necked flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with argon after cooling to room temperature. To this flask were added 1,2-diphenylethyne **1a** (356mg, 2.0 mmol) and K_2S **2a** (221mg, 2.0 mmol), dry DMF (8 mL) under a stream of argon. The flask was heated at 130 ℃ for 12 h. After cooling the reaction mixture to room temperature, the mixture was extracted with ethyl acetate, dried over with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography using n-hexane on silica gel to afford tetraphenylthiophene **3a** (253mg, 65% yield) as a white solid.

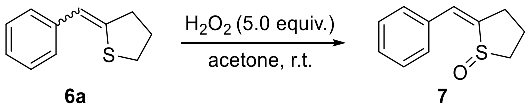
A 50-mL two-necked flask, containing a magnetic stirring bar, was flame-dried under vacuum and filled with Argon after cooling to room temperature. To this flask were tetraphenylthiophene **3a** (253 mg, 0.65 mmol, 1.0 equiv) and dry CH_2Cl_2 (3.0 mL). After cooling to –20 ℃, BF_3 OEt_2 (816 μL, 6.5 mmol, 10 equiv) was added under a stream of Argon. After stirring the mixture at –20 ℃ for 1 h, a solution of m-CPBA (0.65 mmol, 1.0 equiv) in CH_2Cl_2 (1.5 mL) was slowly added (four times every hour), and the resultant mixture was further stirred at –20 ℃ for 1 h. The reaction was quenched by adding saturated $Na_2S_2O_3$ aqueous solution and saturated $NaHCO_3$ aqueous solution. The mixture was extracted with CH_2Cl_2, dried over with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography ($CHCl_3$) to afford 2,3,4,5-tetraphenylthiophene 1-oxide **3a'** (158 mg, 60% yield) as a yellow solid.

A 25-mL screw cap tube, containing a magnetic stirring bar, was flame-dried under vacuum and filled with Argon after cooling to room temperature. To this tube were added **3a'** (162 mg, 0.4 mmol, 1.0 equiv), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (358 mg, 1.2 mmol, 3.0 equiv) and THF (2.0 mL) under a stream of nitrogen. Tetrabutylammonium fluoride (TBAF: 2.4 mL, 2.4 mmol, 6.0 equiv, 1M in THF) was slowly added. The reaction mixture was stirred at room temperature for 24 h. After adding water (20 mL) and CH_2Cl_2 (20 mL) to the mixture, cooling the resultant was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the volatiles were removed under reduced pressure. The volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 10:1) to afford 1,2,3,4-Tetraphenylnaphthalene **4** (142 mg, 82% yield) as a white solid.

4. Synthesis of 2-benzylidenetetrahydrothiophene 6a and (*Z*)-2-benzylidenetetrahydrothiophene 1-oxide 7



A mixture of (cyclopropylethynyl)benzene **5a** (0.50 mmol) and Na_2S $9H_2O$ **2b** (1.0 mmol) in 2.5 mL DMA was stirred at 150 ℃ for 9 h. After completion of the reaction, as indicated by TLC, water (10 mL) was added, and the solution was extracted with ethyl acetate (3 × 15 mL). The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography using n-hexane on silica gel to afford **6a** in 69% yield. All remaining 2-benzylidenetetrahydrothiophene were prepared using a procedure similar to that used to synthesize **6a**.



A 25-mL test tube which contains a magnetic stirring bar were added **6a** (88 mg, 0.5 mmol, 1.0 equiv), and acetone (3.0 mL). H_2O_2 (2.5 mmol, 5.0 equiv, 30% in water) was slowly added at 0 ℃. Then the reaction mixture was stirred at room temperature for 24 h. Water (10 mL) was added, and the solution was extracted with ethyl acetate (3 × 15 mL). The organic layer was dried over Na_2SO_4 and the volatiles were removed under reduced pressure. The volatiles were removed under reduced pressure. The residue was purified by flash column chromatography using ethyl acetate on silica gel to afford (*Z*)-2-benzylidenetetrahydrothiophene 1-oxide **7** (82 mg, 85% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.32 (m, 3H), 7.09 (s, 1H), 3.15 (dq, *J* = 8.3, 6.0, 4.4 Hz, 2H), 2.86 – 2.62 (m, 3H), 2.22 – 2.10 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 135.9, 135.3, 129.2, 128.9, 128.7, 54.5, 33.3, 23.2.

5. Screenings of two Reactions' Conditions

Table 1. Optimization of the cycloaddition reaction conditions

Entry	Sulfur reagents (mmol)	Solvent (2.5 mL)	Temperature (°C)	LC-Yield[b] (%)
1	K_2S (0.36)	DMF	120	65(48)[c]
2	$Na_2S·9H_2O$ (0.36)	DMF	120	36
3	S_8+NaO^{t}Bu (0.36)	DMF	120	trace
4	$Na_2S_2O_3$ (0.36)	DMF	120	N.D
5	Thiourea(0.36)	DMF	120	N.D
6	K_2S (0.36)	DMSO	120	52
7	K_2S (0.36)	DMA	120	40
8	K_2S (0.36)	Toluene	120	trace
9	K_2S (0.36)	H_2O	120	N.D[d]
10	K_2S (0.36)	CH_3CN	120	<10
11	K_2S (0.36)	DMF	r.t.	N.D
12	K_2S (0.36)	DMF	80	N.D
13	K_2S (0.36)	DMF	110	49
14	K_2S (0.36)	DMF	130	70(63)[c]
15	K_2S (0.36)	DMF	140	68
16	K_2S (0.36)	DMF	150	69
17	K_2S (0.45)	DMF	130	73
18	K_2S (0.6)	DMF	130	78(69)[c]
19	K_2S (0.9)	DMF	130	78
20	K_2S (1.2)	DMF	130	77

[a]Reaction Conditions: **1a** (0.6 mmol), Sulfur reagents (X mmol), solvent (2.5 mL) under argon atmosphere for 12 h. [b]The yields were determined by LC analysis using biphenyl as the internal standard. [c]Isolated yields. [d]N.D. = no target product detected.

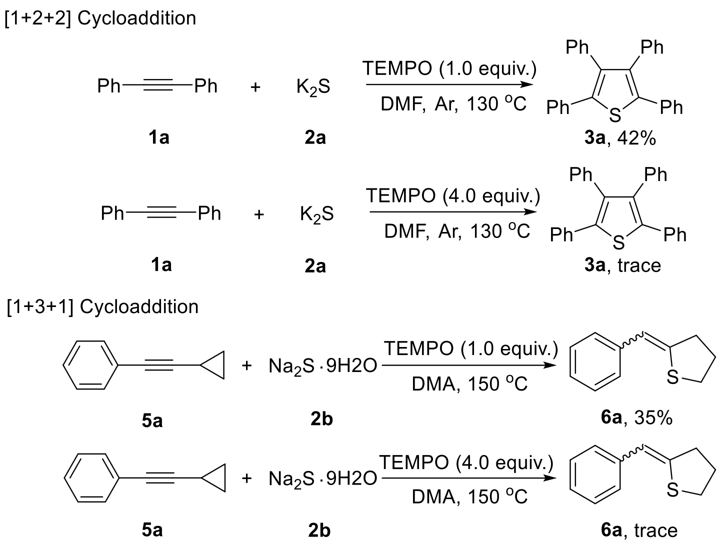
Table 2. Optimization of the ring expansion reaction conditions

Entry	Sulfur reagents (equiv.)	Slovent (2.5 mL)	Tempurature (°C)	LC-Yield[b] (%)
1	K_2S (2.0)[e]	DMF	130	48(35)[c]
2	K_2S (2.0)	DMF	130	60
3	$Na_2S·9H_2O$ (2.0)	DMF	130	67(56)[c]
4	S_8+NaO^{t}Bu (2.0)	DMF	130	trace
5	$Na_2S_2O_3$ (2.0)	DMF	130	N.D
6	Thiourea(2.0)	DMF	130	N.D

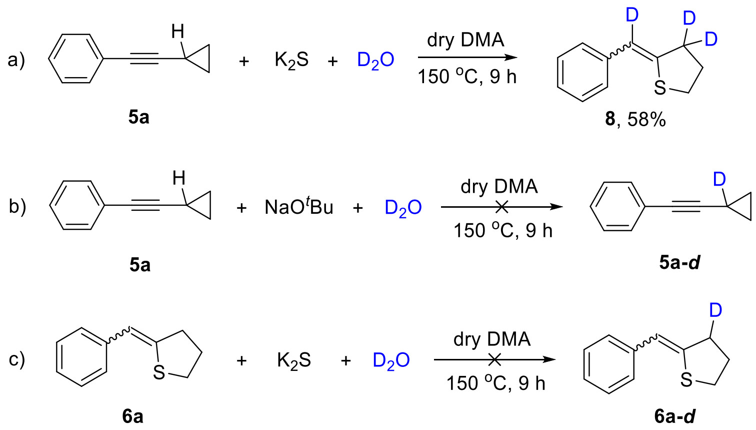
7	$Na_2S{\cdot}9H_2O$ (2.0)	DMSO	130	40
8	$Na_2S{\cdot}9H_2O$ (2.0)	DMA	130	trace
9	$Na_2S{\cdot}9H_2O$ (2.0)	toluene	130	N.D
10	$Na_2S{\cdot}9H_2O$ (2.0)	DMA	140	73
11	$Na_2S{\cdot}9H_2O$ (2.0)	DMA	150	79(69)[c]
12	$Na_2S{\cdot}9H_2O$ (2.0)	DMA	160	70
13	$Na_2S{\cdot}9H_2O$ (2.0)	NMP[f]	160	N.D
14	$Na_2S{\cdot}9H_2O$ (2.0)	Mesitylene	170	N.D
15	$Na_2S{\cdot}9H_2O$ (1.5)	DMA	150	71
16	$Na_2S{\cdot}9H_2O$ (3.0)	DMA	150	79

[a]Reaction Conditions: **5a** (0.5 mmol), **Sulfur reagents** (X equiv.), solvent (2.5 mL) for 9 h. [b]The yields were determined by LC analysis using biphenyl as the internal standard. [c]Isolated yields. [d]N.D. = no target product detected. [e]The reaction was conducted under argon atmosphere. [f]NMP = 1-Methyl-2-pyrrolidinone.

6. Radical-trapping experiments



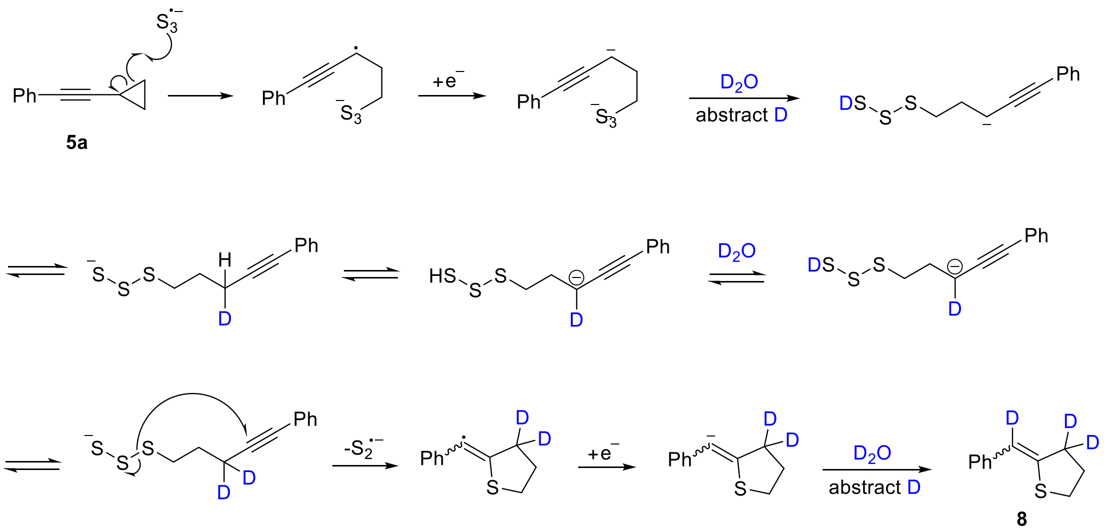
7. Investigation of the Hydrogen Source in [1+3+1] cycloaddition Reaction



As shown as above, 2-(phenylmethylene-*d*)tetrahydrothiophene-3,3-d_2 **8** was formed in 58% yield when $Na_2S\cdot 9H_2O$ was replaced by K_2S and D_2O. This result indicated that water was the hydrogen donor in the transformation. Then, The other two experiments showed that the reaction product **8** was achieved by the following reaction pathway.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.25 – 7.10 (m, 2H), 6.46 (d, *J* = 19.3 Hz, 0.13H), 3.13 (dt, *J* = 45.6, 6.4 Hz, 2H), 2.87 – 2.67 (m, 0.37H), 2.07 (dt, *J* = 40.7, 6.4 Hz, 2H).

$$Na_2S + DMA \longrightarrow S_3^{\bullet-} + ne^-$$



8. ESR Experiments

EPR Studies of Interaction between $Na_2S\cdot 9H_2O$ and different solvents

Five dried tubes equipped with a stir bar were respectively loaded with $Na_2S\cdot 9H_2O$ (1.0 mmol) in 2.5 mL DMSO, DMF, DMA, NMP and Mesitylene. They were all stirred at 25 ℃. After 2 h, the solution samples were taken by five 0.3mm glass capillaries and analyzed by ESR. ESR spectra was recorded at room temperature on ESR spectrometer operated at 9150.300 MHz. Typical spectrometer parameters are shown as follows, Mod freq = 100 kHz, width = 0. 5000 mT; Field center = 325.571.000 mT, width = +/-15.000 mT; Sweep time = 30 s.

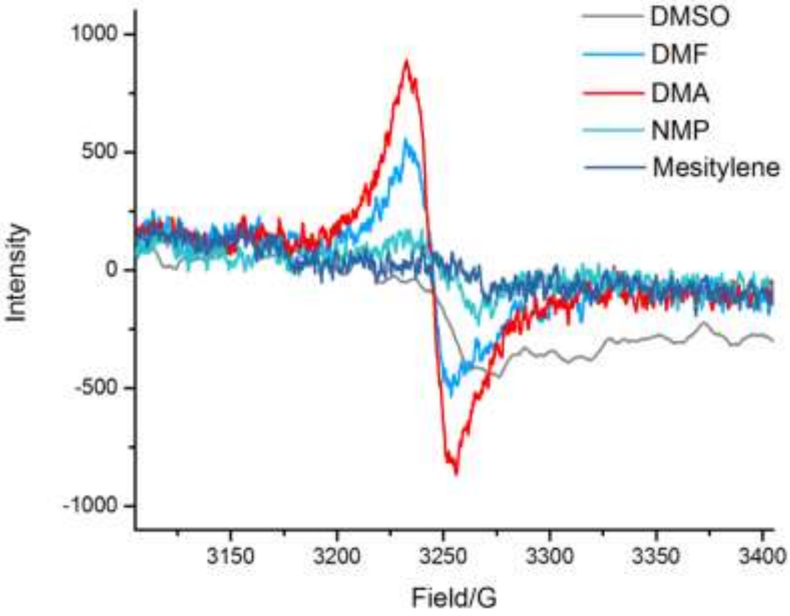
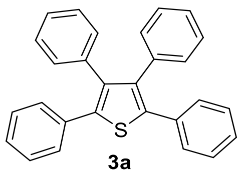


Figure 1. EPR spectra of solutions of $Na_2S{\cdot}9H_2O$ (1.0 mmol) in various solvents (2.5 mL) at 298 K.

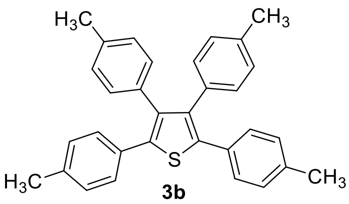
9. Spectroscopic Data of Compounds



3a

2,3,4,5-tetraphenylthiophene (3a)

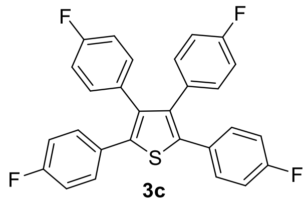
Yield = 69% (80.4 mg). White solid. Mp: 178.5-180.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.18(m, 10H), 7.14 – 7.08 (m, 6H), 6.96 (dd, *J* = 7.8, 1.5 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.6, 138.7, 136.6, 134.4, 131.0, 129.4, 128.4, 128.0, 127.4, 126.7. **IR (ATR)**: ν = 2923, 1596, 1494, 1441, 1030, 916, 793, 748, 706, 693 cm^{-1}; **HRMS** (EI): calcd. for $C_{28}H_{20}S$ $[M+H]^+$: 389.1364, found: 389.1358.



3b

2,3,4,5-tetra-p-tolylthiophene (3b)

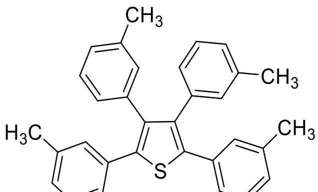
Yield = 81% (108.0 mg). Pale brown solid. **Mp**: 220.0-221.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.9 Hz, 4H), 7.01 (d, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 7.9 Hz, 4H), 6.84 (d, *J* = 7.8 Hz, 4H), 2.29 (s, 6H), 2.26 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 138.1, 136.9, 136.0, 133.8, 131.8, 130.8, 129.1(5), 129.1(2), 128.7, 21.3(8), 21.3(1). **IR (ATR)**: ν = 2920, 1514, 1495, 1182, 1019, 833, 733, 685 cm^{-1}; **HRMS** (EI): calcd. for $C_{32}H_{28}S$ $[M+H]^+$: 445.1990, found: 445.1989.



3c

2,3,4,5-tetrakis(4-fluorophenyl)thiophene (3c)

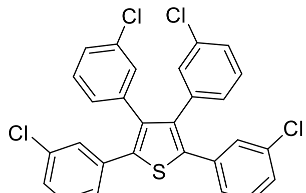
Yield = 28% (38.7 mg). White solid. **Mp**: 175.9-177.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 4H), 6.98 – 6.79 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 163.1, 161.1, 160.7, 138.4, 137.8, 132.5, 132.4, 132.1, 132.0, 131.1, 131.0, 130.0(3), 129.9(9), 115.8 115.6, 115.4, 115.2. **IR (ATR)**: ν = 2921, 1602, 1491, 1220, 1160, 1013, 812, 547, 513 cm^{-1}; **HRMS** (EI): calcd. for $C_{28}H_{16}F_4S$ $[M+H]^+$: 461.0987, found: 461.0975.



3d

2,3,4,5-tetra-m-tolylthiophene (3d)

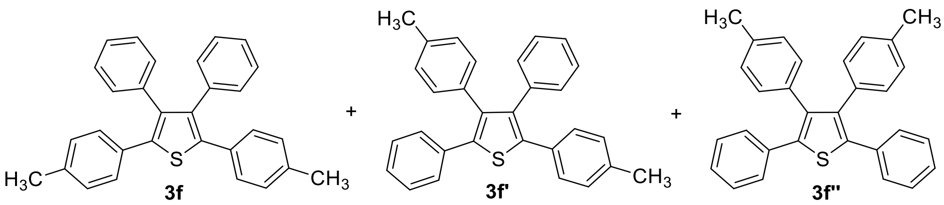
Yield = 86% (114,7 mg). Brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, J = 1.9 Hz, 2H), 7.11 – 6.93 (m, 10H), 6.80 (d, J = 8.8 Hz, 4H), 2.27 (s, 6H), 2.16 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.8, 138.3, 137.9, 137.2, 136.7, 134.4, 131.7, 129.9, 128.2, 128.0(4), 127.9(5), 127.6, 127.3, 126.3, 21.5, 21.4. **IR (ATR)**: ν = 2918, 1601, 1451, 1091, 882, 779, 692, 483 cm^{-1}; **HRMS** (EI): calcd. for $C_{32}H_{28}S$ $[M+H]^+$: 445.1990, found: 445.1981.



3e

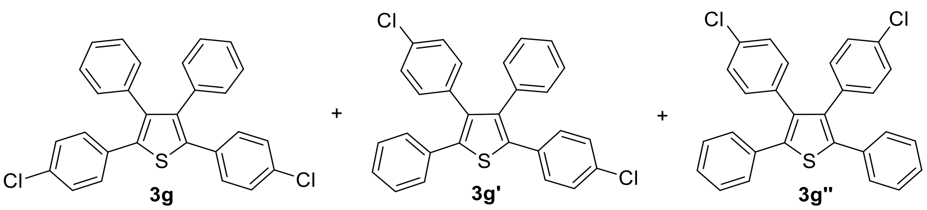
2,3,4,5-tetrakis(3-chlorophenyl)thiophene (3e)

Yield = 73% (115.3 mg). Reddish brown solid. **Mp**: 49.3-52.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.01 (m, 12H), 6.95 (t, J = 1.8 Hz, 2H), 6.84 (dt, J = 7.7, 1.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.5, 138.3, 137.4, 135.2, 134.5, 134.1, 130.6, 129.8, 129.6, 129.2 129.0, 128.0, 127.6, 127.4. **IR (ATR)**: ν = 2922, 1561, 1465, 1260, 1077, 883, 775, 697, 441 cm^{-1}; **HRMS** (EI): calcd. for $C_{28}H_{16}Cl_4S$ $[M+H]^+$: 524.9805, found: 524.9789.



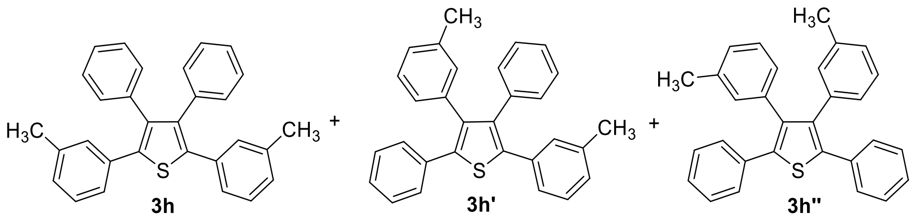
Mixture of 3,4-diphenyl-2,5-di-p-tolylthiophene (3f) and 2,4-diphenyl-3,5-di-p-tolylthiophene (3f’) and 2,5-diphenyl-3,4-di-p-tolylthiophene (3f’’)

Total yield = 51% (63.7 mg). White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 5H), 7.14 – 7.06 (m, 5H), 7.04 – 6.93 (m, 4H), 6.90 (dd, *J* = 7.8, 5.1 Hz, 2H), 6.86 – 6.81 (m, 2H), 2.28 (s, 3H), 2.24 (d, *J* = 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.6, 139.5(5), 139.3, 139.2, 138.8, 138.4(4), 138.3(7), 138.0, 137.0(9), 137.0(7), 136.8(8), 136.8(2), 136.1(8), 136.1(5), 134.6(2), 134.6(1), 133.5(9), 133.5(4), 131.5, 131.0(3), 131.0(1), 130.8(2), 130.8(0), 129.3(4), 129.3(3), 129.2, 128.7(2), 128.7(0), 128.4, 127.9(4), 127.9(3), 127.2, 127.1(8), 126.6(1), 126.6(0), 21.3(7), 21.3(4), 21.3(0). **IR (ATR)**: ν = 2919, 1672, 1542, 1484, 1181, 1072, 814, 751, 694 cm^{-1}; **HRMS** (EI): calcd. for $C_{30}H_{24}S$ $[M+H]^+$: 417.1677, found: 417.1678.



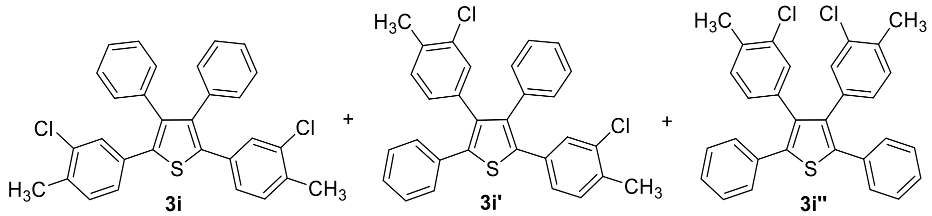
Mixture of 2,5-bis(4-chlorophenyl)-3,4-diphenylthiophene (3g) and 2,4-bis(4-chlorophenyl)-3,5-diphenylthiophene (3g’) and 3,4-bis(4-chlorophenyl)-2,5-diphenylthiophene (3g’’)

Total yield = 70% (96.1 mg). White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.04 (m, 14H), 6.93 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.86 (dd, *J* = 8.4, 1.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.1, 139.7, 139.4(1), 139.3(9), 138.2, 137.8, 137.5, 136.0(8), 136.0(3), 134.8, 134.7(6), 133.8(6), 133.8(5), 133.4(3), 133.4(1), 133.0, 132.8, 132.6(9), 132.6(8), 132.2, 130.8, 130.5, 129.4, 128.7, 128.6, 128.5, 128.3(2), 128.3(1), 128.2, 127.7(1), 127.6(9), 127.2, 127.0. **IR (ATR)**: ν = 2920, 1597, 1541, 1182, 1073, 833, 749, 696 cm^{-1}; **HRMS** (EI): calcd. for $C_{28}H_{28}Cl_2S$ $[M+H]^+$: 457.0585, found: 457.0578.



Mixture of 3,4-diphenyl-2,5-di-m-tolylthiophene (3h) and 2,4-diphenyl-3,5-di-m-tolylthiophene (3h’) and 2,5-diphenyl-3,4-di-m-tolylthiophene (3h’’)

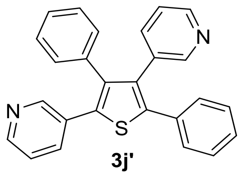
Total yield = 26% (32.5 mg). White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.04 (m, 10H), 7.02 – 6.88 (m, 6H), 6.76 (d, *J* = 6.9 Hz, 2H), 2.22 (s, 3H), 2.10 (d, *J* = 3.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.8, 139.6(9), 139.6(2), 139.5, 138.7(2), 138.6(6), 138.3(6), 138.3(1), 138.0, 137.3, 137.2, 136.7(8), 136.7(3), 136.5(0), 136.4(6), 134.5(2), 134.5(0), 134.3, 131.7, 130.9(7), 130.9(6), 130.0, 129.2, 128.4, 128.2, 128.0(7), 128.0(4), 127.9(0), 127.8(5), 127.7(5), 127.7, 127.4(1), 127.3(8), 127.2, 126.6(4), 126.6(2), 126.4, 21.5, 21.4. **IR (ATR)**: ν =2924, 1742, 1601, 1442, 906, 751, 693, 440 cm^{-1}; **HRMS** (EI): calcd. for $C_{30}H_{24}S$ $[M+H]^+$: 417.1677, found: 417.1678.



3i 3i' 3i''

Mixture of 2,5-bis(3-chloro-4-methylphenyl)-3,4-diphenylthiophene (3i) and 2,4-bis(3-chloro-4-methylphenyl)-3,5-diphenylthiophene (3i') and 3,4-bis(3-chloro-4-methylphenyl)-2,5-diphenylthiophene (3i'')

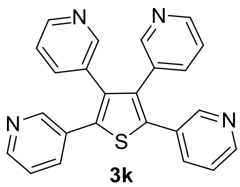
Total yield = 75% (109.2 mg). White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.24 (m, 9H), 7.20 – 7.02 (m, 6H), 6.95 – 6.84 (m, 1H), 2.54 – 2.31 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.0, 139.8, 139.2, 137.9, 137.7, 137.1(8), 137.1(6), 136.1(4), 136.0(8), 135.4(8), 135.4(4), 135.1(2), 135.0(9), 134.5, 134.3(8), 134.3(6), 133.9(2), 133.8(9), 133.8(8), 133.8(3), 133.4, 131.2(1), 131.1(9), 130.9, 130.7(8), 130.7(6), 130.6, 130.4(8), 129.4(6), 129.2(7), 129.2(4), 129.1(8), 128.5, 128.2, 128.1, 127.6(2), 127.5(8), 127.3(6), 127.3(5), 127.1, 127.0, 19.8(9), 19.8(7), 19.8(6). **IR (ATR)**: ν = 2921, 1599, 1479, 1050, 882, 818, 753, 694, 442 cm^{-1}; **HRMS** (EI): calcd. for $C_{30}H_{22}Cl_2S$ $[M+H]^+$: 485.0898, found: 485.0888.



3j'

3,3'-(3,5-diphenylthiophene-2,4-diyl)dipyridine (3j')

Yield = 51% (59.7 mg). Yellow solid. Mp: 158.2-160.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.2 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.38 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.23 (d, *J* = 2.1 Hz, 1H), 7.46 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.25 (dq, *J* = 5.8, 3.6, 3.1 Hz, 6H), 7.20 – 7.11 (m, 4H), 7.05 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.96 (dd, *J* = 7.5, 2.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 149.7, 148.4, 147.9, 141.2, 140.7, 138.2, 136.3, 135.8, 135.2, 135.1, 133.3, 132.2, 130.8, 130.2, 129.5, 128.8, 128.6, 128.1, 127.6, 123.2, 122.9. **IR (ATR)**: ν = 2921, 1562, 1403, 1260, 1073, 1021, 798, 757, 700, 593 cm^{-1}; **HRMS** (EI): calcd. for $C_{26}H_{18}N_2S$ $[M+H]^+$: 391.1269, found: 391.1276.

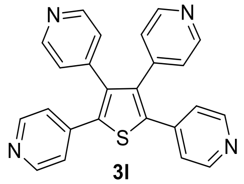


3k

3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl)tetrapyridine (3k)

Yield = 83% (97.7 mg). Yellow solid. Mp: 153.2-155.3 ℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.50 – 8.28 (m, 6H), 8.16 (d, *J* = 2.2 Hz, 2H), 7.42 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.23 – 6.99 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.9, 149.6, 149.0, 148.6, 137.8, 137.4, 136.8, 136.3, 130.8, 129.0, 123.3, 123.2. **IR**

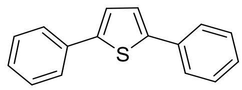
(ATR): ν = 2923, 1562, 1479, 1405, 1181, 1022, 794, 710, 616 cm^{-1}; **HRMS** (EI): calcd. for $C_{24}H_{16}N_4S$ $[M+H]^+$: 393.1174, found: 393.1180.



3l

4,4',4'',4'''-(thiophene-2,3,4,5-tetrayl)tetrapyridine (3l)

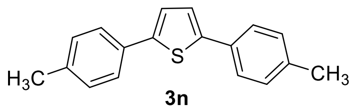
Yield = 73% (86.2 mg). Maroon solid. Mp: 234.2-236.7 ℃. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49 – 8.32 (m, 8H), 7.07 – 6.97 (m, 4H), 6.88 – 6.73 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.2, 150.0, 142.6, 140.0, 138.9, 138.0, 125.0, 123.0. **IR (ATR)**: ν = 2922, 1584, 1540, 1408, 1064, 990, 831, 724, 596, 515 cm^{-1}; **HRMS** (EI): calcd. for $C_{24}H_{16}N_4S$ $[M+H]^+$: 393.1174, found: 393.1175.



3m, 3o (3m = 3o)

2,5-diphenylthiophene (3m, 3o)

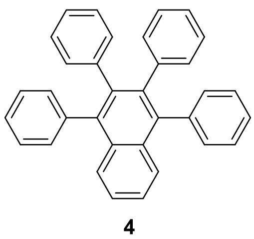
Yield = 27% (19.1 mg). Pale yellow solid. **Mp**: 142.3-143.6 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 8.2, 1.7 Hz, 4H), 7.42 – 7.36 (m, 4H), 7.33 – 7.26 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 134.5, 129.1, 127.7, 125.8, 124.1. **IR (ATR)**: ν = 2923, 1596, 1454, 1260, 1078, 1028, 804, 747, 684 cm^{-1}; **HRMS** (EI): calcd. for $C_{16}H_{12}S$ $[M+H]^+$: 237.0738, found: 237.0735.



3n

2,5-di-p-tolylthiophene (3n)

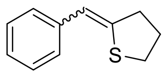
Yield = 36% (28.6 mg). Pale yellow solid. **Mp**: 162.3-163.9 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 4H), 7.24 – 7.15 (m, 6H), 2.36 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 137.4, 131.8, 129.7, 125.6, 123.6, 21.3. **IR (ATR)**: ν =2913, 1498, 1455, 1277, 1125, 940, 821, 796 cm^{-1}; **HRMS** (EI): calcd. for $C_{18}H_{16}S$ $[M+H]^+$: 265.1051, found: 265.1055.



4

1,2,3,4-tetraphenylnaphthalene (4)

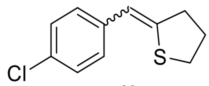
Total yield = 32% (41.5 mg). White solid. **Mp**: 191.9-193.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.37 (dd, *J* = 6.5, 3.3 Hz, 2H), 7.26 – 7.16 (m, 10H), 6.92 – 6.76 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.6, 139.7, 139.0, 138.5, 132.1, 131.4, 127.7, 127.1, 126.7, 126.6, 126.0, 125.5. **IR (ATR)**: ν = 1924, 1600, 1440, 1029, 743, 695, 582, 560, 500 cm^{-1}; **HRMS** (EI): calcd. for $C_{34}H_{24}$ $[M+H]^+$: 433.1956, found: 433.1961.



6a

2-benzylidenetetrahydrothiophene (*E/Z*= 24:76) (6a)

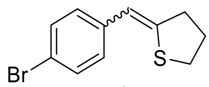
Yield = 69% (60.8 mg). Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 1H), 7.35 – 7.24 (m, 2H), 7.24 – 7.10 (m, 1H), 6.46 (s, 0.76×1H), 6.42 (t, *J* = 1.9 Hz, 0.24×1H), 3.14 (t, *J* = 6.4 Hz, 0.76×2H), 3.03 (t, *J* = 6.4 Hz, 0.24×2H), 2.84 – 2.74 (m, 2H), 2.12 – 2.05 (m, 0.24×2H), 1.98 (p, *J* = 6.6 Hz, 0.76×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.6, 143.2, 138.4, 137.8, 128.3, 127.7(2), 127.6(7), 125.7(4), 125.6(6), 117.3, 117.1, 40.3, 35.7, 34.4, 33.0, 31.1, 28.4. **IR (ATR)**: ν = 2928, 1613, 1489, 1442, 1256, 816, 749, 690, 627, 521 cm^{-1}; **HRMS** (EI): calcd. for $C_{11}H_{12}S$ $[M+H]^+$: 177.0738, found: 177.0736.



6b

2-(4-chlorobenzylidene)tetrahydrothiophene (*E/Z*= 5:95) (6b)

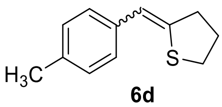
Yield = 72% (75.9 mg). White solid. **Mp**: 42.1-43.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 6.41 (s, 0.95×1H), 6.36 (s, 0.05×1H), 3.19 (t, *J* = 6.4 Hz, 0.95×2H), 3.07 (t, *J* = 6.4 Hz, 0.05×2H), 2.80 (td, *J* = 6.8, 1.5 Hz, 2H), 2.13 (p, *J* = 6.6 Hz, 0.05×2H), 2.02 (p, *J* = 6.6 Hz, 0.95×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 136.4, 131.1, 128.9, 128.5, 115.9, 40.4, 35.8, 28.5. **IR (ATR)**: ν = 2946, 2856, 1612, 1561, 1487, 1403, 1084, 1004, 862, 840, 690, 619 cm^{-1}; **HRMS** (EI): calcd. for $C_{11}H_{11}ClS$ $[M+H]^+$: 211.0348, found: 211.0347.



6c

2-(4-bromobenzylidene)tetrahydrothiophene (*E/Z*= 23:77) (6c)

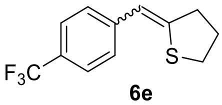
Yield = 66% (84.2 mg). White solid. **Mp**: 40.3-42.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m), 7.32 – 7.27 (m), 7.12 – 7.04 (m), 6.41 (s, 0.77×1H), 6.36 (t, *J* = 2.0 Hz, 0.23×1H), 3.20 (t, *J* = 6.4 Hz, 0.77×2H), 3.09 (t, *J* = 6.4 Hz, 0.23×2H), 2.87 – 2.76 (m, 2H), 2.15 (p, *J* = 6.6 Hz, 0.23×2H), 2.05 (p, *J* = 6.6 Hz, 0.77×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 144.5, 137.3, 136.8, 131.4(3), 131.4(0), 129.2(5), 129.2(3), 119.2(6), 119.2(1), 116.1(0), 115.9(6), 40.4, 35.9, 34.5, 33.1, 31.1, 28.5. **IR (ATR)**: ν = 2926, 1610, 1482, 1398, 861, 838, 798, 666, 518, 444 cm^{-1}; **HRMS** (EI): calcd. for $C_{11}H_{11}BrS$ $[M+H]^+$: 254.9843, found: 254.9841.



6d

2-(4-methylbenzylidene)tetrahydrothiophene (*E/Z*= 13:87) (6d)

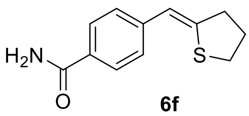
Yield = 52% (49.5 mg). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz), 7.20 – 7.12 (m), 6.48 (s, 0.87×1H), 6.43 (t, *J* = 2.0 Hz, 0.13×1H), 3.20 (t, *J* = 6.4 Hz, 0.87×2H), 3.09 (t, *J* = 6.4 Hz, 0.13×2H), 2.83 (td, *J* = 6.8, 1.5 Hz, 2H), 2.35 (s, 2H), 2.15 (p, *J* = 6.6 Hz, 0.13×2H), 2.05 (p, *J* = 6.6 Hz, 0.87×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 142.0, 135.7, 135.4, 135.3, 135.1, 129.1, 127.6(6), 127.6(2), 117.2, 117.0, 40.2, 35.6, 34.3, 32.9, 31.1, 28.5, 21.2(8), 21.2(2). **IR (ATR)**: ν = 2940, 1601, 1413, 1322, 1107, 1067, 964, 861, 656 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{14}S$ $[M+H]^+$: 191.0894, found: 191.0890.



6e

2-(4-(trifluoromethyl)benzylidene)tetrahydrothiophene (*E/Z*= 30:70) (6e)

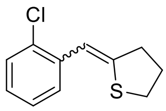
Yield = 68% (83.1 mg). White solid. **Mp**: 47.2-48.1 ℃. **^{1}H NMR** (400 MHz, CDCl3) δ 7.62 – 7.46 (m), 7.28 (d, *J* = 8.2 Hz), 6.49 (s, 0.7×1H), 6.44 (s, 0.3×1H), 3.21 (t, *J* = 6.4 Hz, 0.7×2H), 3.08 (t, *J* = 6.4 Hz, 0.3×2H), 2.91 – 2.76 (m, 2H), 2.15 (p, *J* = 6.6 Hz, 0.3×2H), 2.04 (p, *J* = 6.6 Hz, 0.7×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.2, 147.0, 141.8 (d, *J* = 1.3 Hz), 141.4, 129.5, 129.2, 128.6, 127.7(1), 127.6(7), 127.5, 127.2 (d, *J* = 32.1 Hz), 127.1, 126.8, 125.3 (q, *J* = 7.5 Hz), 124.5 (d, *J* = 270 Hz), 120.5, 115.9, 115.8, 40.6, 36.0, 34.7, 33.1, 31.2, 28.4. **IR (ATR)**: ν = 2940, 1601, 1413, 1322, 1107, 1067, 964, 861, 656 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{11}F_3S$ $[M+H]^+$: 245.0612, found: 245.0608.



6f

(*Z*)-4-((dihydrothiophen-2(3H)-ylidene)methyl)benzamide (6f)

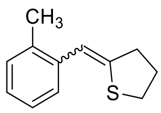
Yield = 48% (52.6 mg). White solid. **Mp**: 165.3-166.1 ℃. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.07 – 7.68 (m, 3H), 7.52 – 7.14 (m, 3H), 6.55 (s, 1H), 3.19 (s, 2H), 2.80 (s, 2H), 1.94 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.6, 146.3, 140.3, 131.0, 127.7, 126.7, 115.7, 40.0, 35.4, 28.0. **IR (ATR)**: ν = 3394, 3173, 1641, 1598, 1556, 1386, 866, 759, 630 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{13}NOS$ $[M+H]^+$: 220.0796, found: 220.0798.



6g

(*Z*)-2-(2-chlorobenzylidene)tetrahydrothiophene (6g)

Yield = 45% (47.4 mg). Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.09 (td, *J* = 7.7, 1.5 Hz, 1H), 6.76 (s, 1H), 3.18 (t, *J* = 6.4 Hz, 2H), 2.87 (td, *J* = 6.9, 1.6 Hz, 2H), 2.06 (p, *J* = 6.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 135.8, 132.8, 129.5, 128.4, 127.0, 126.6, 113.3, 40.3, 35.4, 28.5. **IR (ATR)**: ν = 2925, 1607, 1433, 1256, 1034, 748, 692, 622, 469, 422 cm^{-1}; **HRMS** (EI): calcd. for $C_{11}H_{11}ClS$ $[M+H]^+$: 211.0348, found: 211.0350.

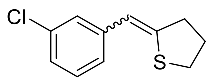


6h

2-(2-methylbenzylidene)tetrahydrothiophene (*E/Z*= 18:82) (6h)

Yield = 68% (64.7 mg). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz), 7.26 – 7.01

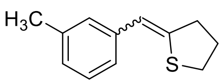
(m), 6.52 (s, 0.82×1H), 6.44 (s, 0.18×1H), 3.09 (t, *J* = 6.4 Hz, 0.82×2H), 3.05 (t, *J* = 6.4 Hz, 0.18×2H), 2.79 (td, *J* = 6.8, 1.6 Hz, 0.82×2H), 2.69 (td, *J* = 6.8, 2.1 Hz, 0.18×2H), 2.28 (s, 0.82×3H), 2.25 (s, 0.18×3H), 2.02 (dp, J = 19.9, 6.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 144.0, 137.5, 136.8, 135.7, 135.5, 123.0, 129.9, 128.1, 127.1, 126.2, 125.7, 125.6, 115.7, 114.6, 39.8, 34.9, 34.3, 33.1, 30.7, 28.6, 20.1. **IR (ATR)**: ν = 2947, 1597, 1481, 1256, 1007, 746, 718, 626, 647 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{14}S$ $[M+H]^+$: 191.0894, found: 191.0891.



6i

(*Z*)-2-(3-chlorobenzylidene)tetrahydrothiophene (6i)

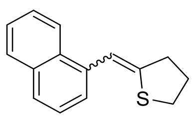
Yield = 30% (31.6 mg). Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.6 Hz, 1H), 7.25 (dq, *J* = 13.8, 7.9 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.41 (s, 1H), 3.20 (t, *J* = 6.4 Hz, 2H), 2.83 (td, *J* = 6.8, 1.4 Hz, 2H), 2.04 (p, *J* = 6.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.4, 139.7, 134.3, 129.6, 127.6, 125.7, 125.7, 115.8, 40.5, 35.9, 28.5. **IR (ATR)**: ν = 2953, 1722, 1589, 1473, 1254, 1081, 773, 683, 651, 461 cm^{-1}; **HRMS** (EI): calcd. for $C_{11}H_{11}ClS$ $[M+H]^+$: 211.0348, found: 211.0344.



6j

2-(3-methylbenzylidene)tetrahydrothiophene (*E/Z*= 17:83) (6j)

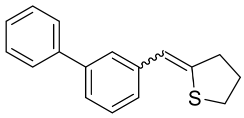
Yield = 68% (64.7 mg). Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.11 (m), 6.98 (dd, *J* = 23.7, 7.3 Hz), 6.42 (s, 0.83×1H), 6.38 (s, 0.17×1H), 3.13 (t, *J* = 6.4 Hz, 0.83×2H), 3.01 (t, *J* = 6.4 Hz, 0.17×2H), 2.78 (dtd, *J* = 8.4, 6.9, 1.8 Hz, 2H), 2.32 (d, *J* = 9.5 Hz, 3H), 2.11 – 2.03 (m, 0.17×2H), 1.97 (p, *J* = 6.6 Hz, 0.83×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 142.9, 137.7(2), 137.6(9), 130.0, 128.5, 128.4, 128.3, 128.2, 127.4, 126.5, 126.4, 126.2, 124.7, 117.2, 117.1, 40.2, 35.6, 34.3, 32.8, 31.1, 28.4, 21.6, 21.4. **IR (ATR)**: ν = 2927, 1599, 1258, 1097, 818, 774, 693, 632, 459 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{14}S$ $[M+H]^+$: 191.0894, found: 191.0891.



6k

2-(naphthalen-1-ylmethylene)tetrahydrothiophene (*E/Z*= 24:76) (6k)

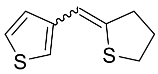
Yield = 60% (67.9 mg). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.87 (m, 1H), 7.71 – 7.60 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.31 (dddd, *J* = 14.0, 12.3, 7.2, 5.4 Hz, 3H), 6.91 (s, 0.76×1H), 6.81 (s, 0.24×1H), 2.92 (t, *J* = 6.4 Hz, 2H), 2.70 (td, *J* = 6.9, 1.6 Hz, 0.76×2H), 2.51 (td, *J* = 6.8, 2.1 Hz, 0.24×2H), 1.91 – 1.77 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.9, 145.9, 135.6, 135.0, 133.6(9), 133.6(0), 131.6, 131.3, 128.5, 128.4, 126.7(1), 126.6(5), 125.8(0), 125.7(6), 125.7(3), 125.6(2), 125.6(0), 125.5, 125.3, 125.2, 124.7, 124.0, 114.4, 113.4, 39.6, 34.7, 34.6, 33.3, 30.5, 28.6. **IR (ATR)**: ν = 2928, 1588, 1394, 1254, 1007, 773, 635, 457 cm^{-1}; **HRMS** (EI): calcd. for $C_{15}H_{14}S$ $[M+H]^+$: 227.0894, found: 227.0890.



6l

2-([1,1'-biphenyl]-4-ylmethylene)tetrahydrothiophene (*E/Z*= 15:85) (6l)

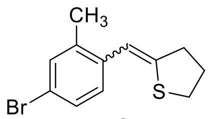
Yield = 76% (95.9 mg). White solid. **Mp**: 81.9-83.4 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (ddd, *J* = 25.3, 12.8, 4.8 Hz, 6H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.27 (m, 1H), 6.52 (s, 0.85×1H), 6.47 (s, 0.15×1H), 3.22 (t, *J* = 6.4 Hz, 0.85×2H), 3.10 (t, *J* = 6.4 Hz, 0.15×2H), 2.87 (dtd, *J* = 8.2, 6.9, 1.8 Hz, 2H), 2.17 (p, *J* = 6.6 Hz, 0.15×2H), 2.06 (p, *J* = 6.6 Hz, 0.85×2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.9, 143.6, 141.0, 140.8, 138.3, 137.5, 137.0, 128.8, 128.1, 127.2, 127.1, 127.0(1), 126.9(7), 116.9, 116.7, 40.4, 35.8, 34.5, 33.0, 31.2, 28.5. **IR (ATR)**: ν = 2927, 1611, 1482, 1406, 1257, 1076, 1012, 864, 757, 687, 552, 500 cm^{-1}; **HRMS** (EI): calcd. for $C_{17}H_{16}S$ $[M+H]^{+}$: 253.1051, found: 253.1048.



6m

3-((dihydrothiophen-2(3H)-ylidene)methyl)thiophene (*E/Z*= 14:86) (6m)

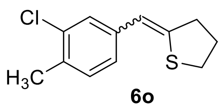
Yield = 68% (62.0 mg). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (ddd, *J* = 7.5, 6.9, 4.3 Hz), 7.15 (dd, *J* = 4.9, 1.3 Hz), 7.01 (dd, *J* = 5.0, 1.2 Hz), 6.96 (d, *J* = 2.7 Hz), 6.50 (s, 0.88×1H), 6.42 (t, *J* = 1.9 Hz, 0.12×1H), 3.16 (t, *J* = 6.4 Hz, 0.88×2H), 3.04 (t, *J* = 6.4 Hz, 0.12×2H), 2.83 – 2.68 (m, 2H), 2.07 (dp, *J* = 42.7, 6.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 142.6, 139.6, 139.3, 128.1, 127.8, 124.9, 124.8, 120.5, 120.0, 111.7, 111.4, 39.4, 35.5, 34.5, 33.3, 31.0, 28.9. **IR (ATR)**: ν = 2928, 1616, 1259, 1078, 1008, 815, 758, 624, 609, 448 cm^{-1}; **HRMS** (EI): calcd. for $C_9H_{10}S_2$ $[M+H]^{+}$: 183.0302, found: 183.0304.



6n

2-(4-bromo-2-methylbenzylidene)tetrahydrothiophene (*E/Z*= 21:79) (6n)

Yield = 65% (87.5 mg). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz), 7.37 – 7.15 (m, 2H), 7.01 (d, *J* = 8.1 Hz), 6.41 (s, 0.79×1H), 6.32 (s, 0.21×1H), 3.11 (t, *J* = 6.4 Hz, 0.79×2H), 3.06 (t, *J* = 6.4 Hz, 0.21×2H), 2.78 (td, *J* = 6.8, 1.6 Hz, 0.79×2H), 2.64 (td, *J* = 6.8, 2.1 Hz, 0.21×2H), 2.22 (d, *J* = 9.9 Hz, 3H), 2.12 – 1.93 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 145.1, 137.9, 137.7, 136.4, 135.8, 132.6(4), 132.6(0), 129.5, 128.6(7), 128.6(0), 128.5, 119.5, 119.4, 114.4, 113.5, 39.9, 35.1, 34.3, 33.2, 30.7, 28.6, 19.9(2), 19.9(0). **IR (ATR)**: ν = 2929, 1610, 1475, 1256, 1121, 871, 824, 653, 551, 478 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{13}BrS$ $[M+H]^{+}$: 269.0000, found: 269.0002.

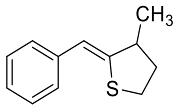


6o

2-(3-chloro-4-methylbenzylidene)tetrahydrothiophene (*E/Z*= 14:86) (6o)

Yield = 57% (64.1 mg). White solid. **Mp**: 69.1-70.6 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.6 Hz), 7.24 – 7.08 (m, 2H), 6.96 (dd, *J* = 7.9, 1.6 Hz), 6.35 (s, 0.86×1H), 6.31 (s, 0.14×1H), 3.15 (t, *J* =

6.4 Hz, 0.86×2H), 3.04 (t, *J* = 6.4 Hz, 0.14×2H), 2.77 (ddd, *J* = 8.3, 5.9, 2.5 Hz, 2H), 2.37 – 2.31 (m, 3H), 2.05 (dp, *J* = 44.2, 6.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 144.1, 137.6, 137.2, 134.2(5), 134.2(2), 133.0(7), 133.0(2), 130.7, 128.0, 127.8, 126.0, 125.7(8), 115.7(4), 115.6, 40.2, 35.7, 34.4, 33.0, 31.1, 28.4, 19.7(8), 19.7(2). **IR (ATR)**: ν = 2931, 1599, 1490, 1256, 1045, 882, 817, 582, 440 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{13}ClS$ [M+H]$^+$: 225.0505, found: 225.0499.

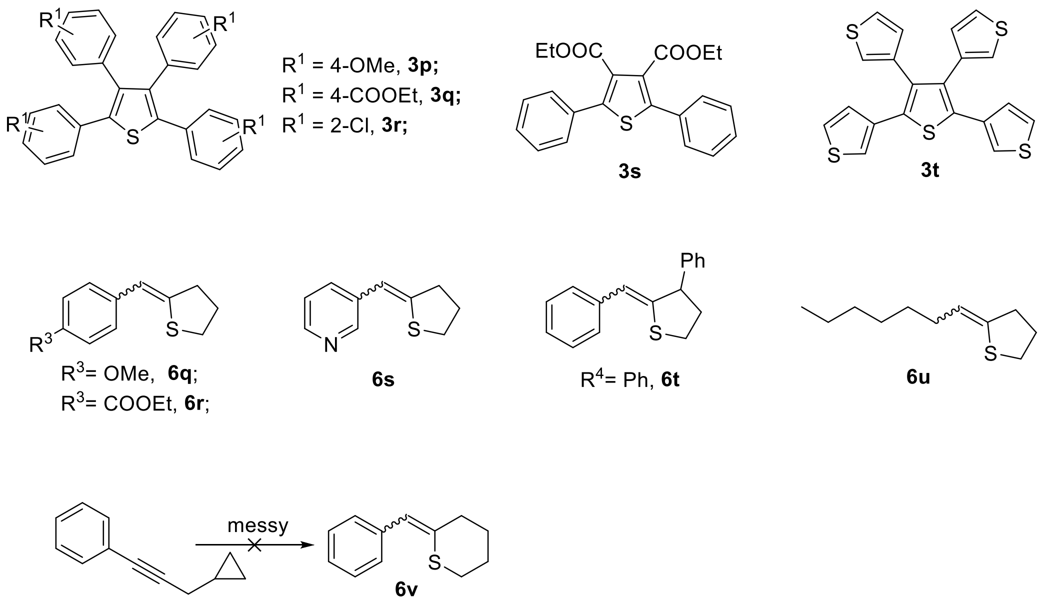


6p

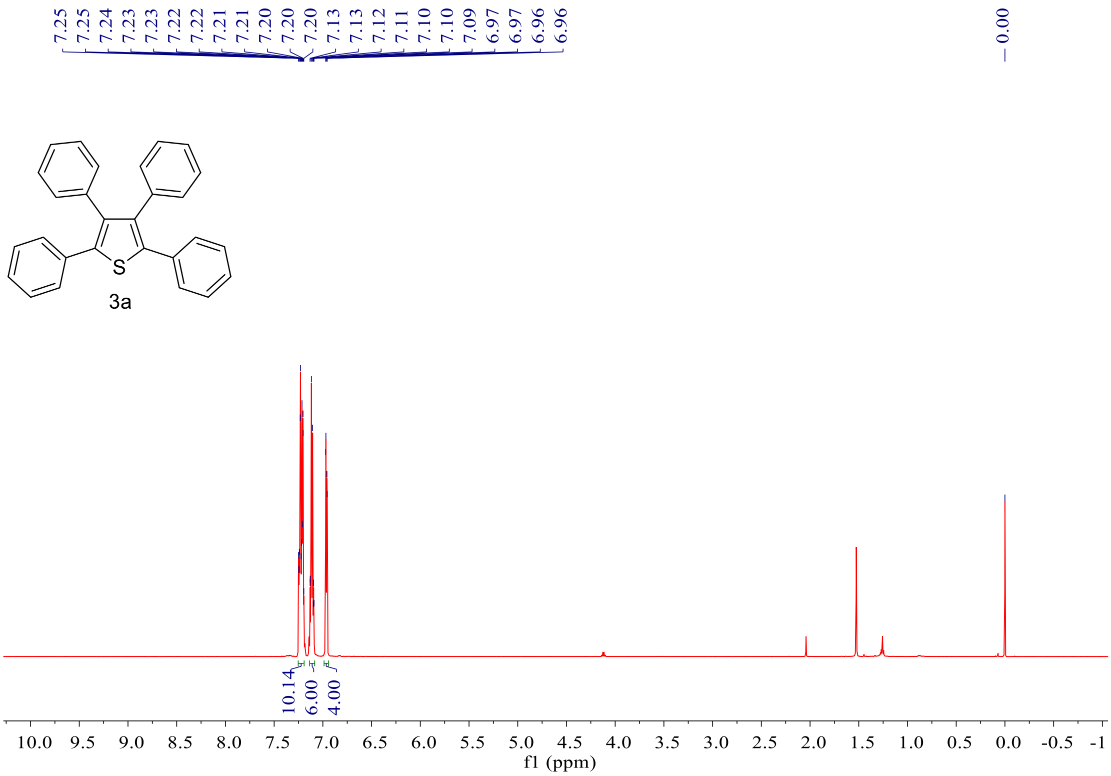
(*Z*)-2-benzylidene-3-methyltetrahydrothiophene (6p)

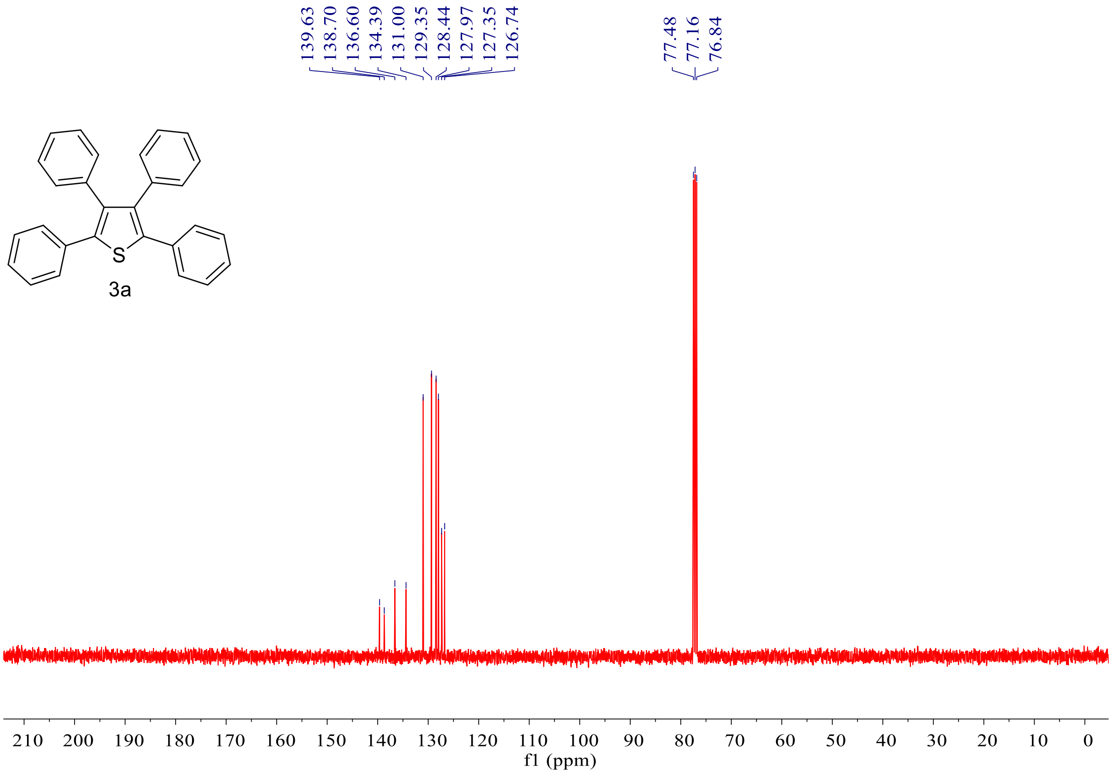
Yield = 36% (34.3 mg). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.42 (s, 1H), 3.24 – 3.09 (m, 2H), 2.98 (dd, *J* = 13.3, 6.6 Hz, 1H), 2.22 (dq, *J* = 11.9, 5.9 Hz, 1H), 1.75 (ddd, *J* = 14.3, 12.4, 7.8 Hz, 1H), 1.32 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 137.4, 127.8, 127.4, 125.3, 115.9, 44.5, 35.9, 31.9, 18.4. **IR (ATR)**: ν = 2926, 1610, 1444, 1255, 1111, 750, 690, 665, 516 cm^{-1}; **HRMS** (EI): calcd. for $C_{12}H_{14}S$ [M+H]$^+$: 191.0894, found: 191.0896.

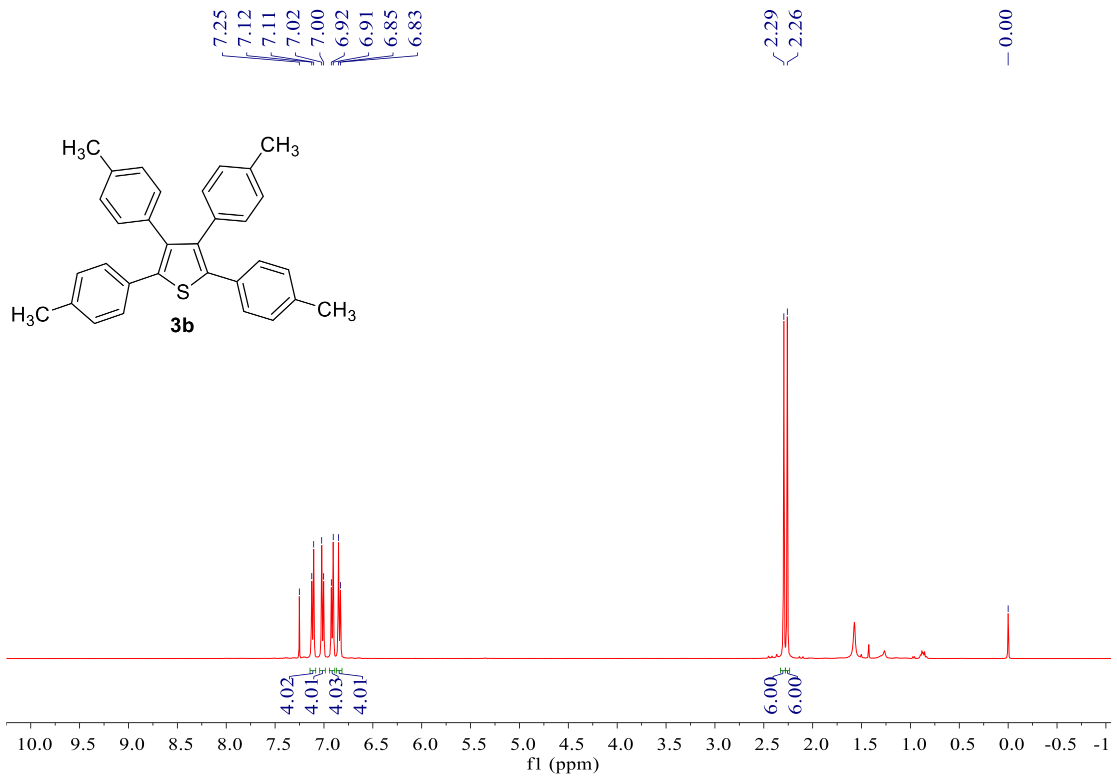
10. Unsuccessful examples

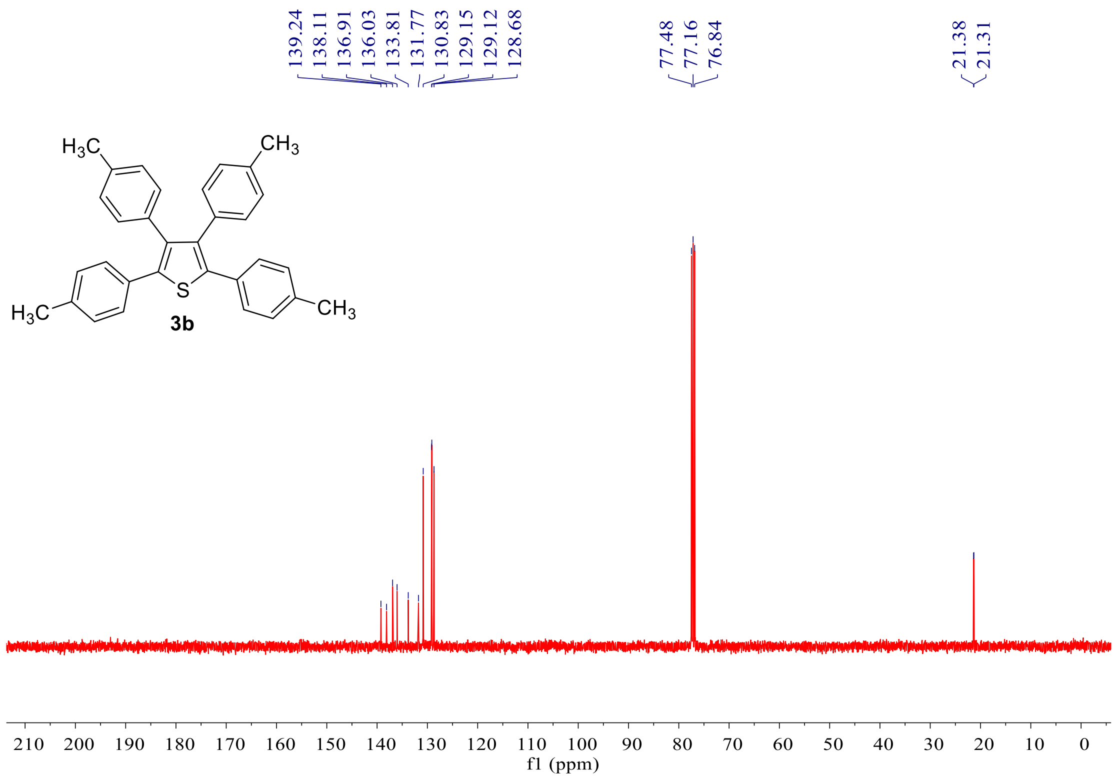


11. Copies of ^{1}H NMR and ^{13}C NMR Spectra for Compounds






7.25
7.12
7.11
7.02
7.00
6.92
6.91
6.85
6.83
2.29
2.26
0.00
H3C
CH3
H3C
CH3
S
3b
4.02
4.01
4.03
4.01
6.00
6.00
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 0.0 -0.5 -1
f1 (ppm)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138.11
136.91
136.03
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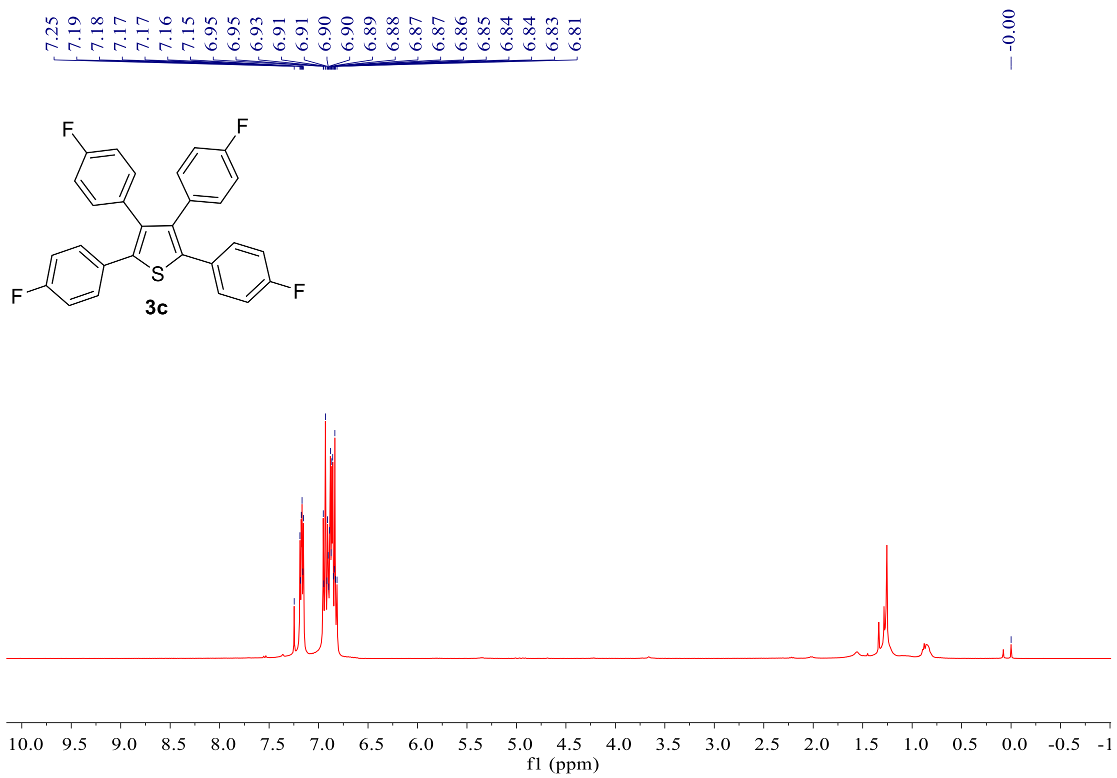
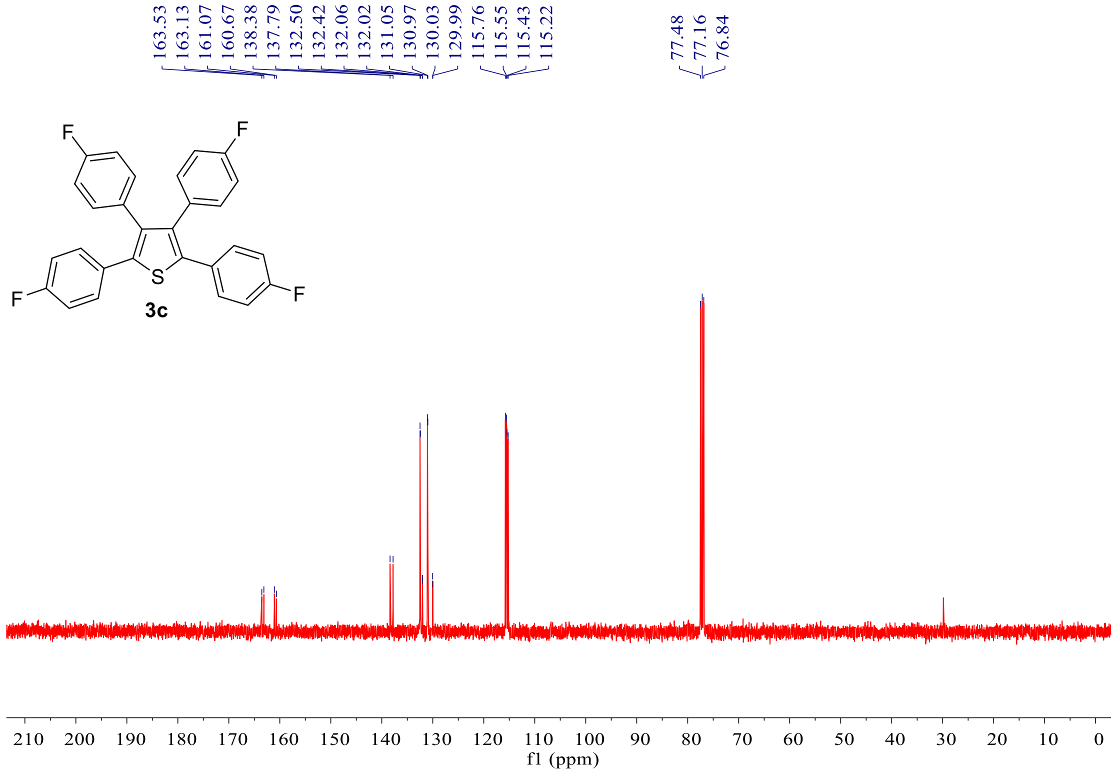
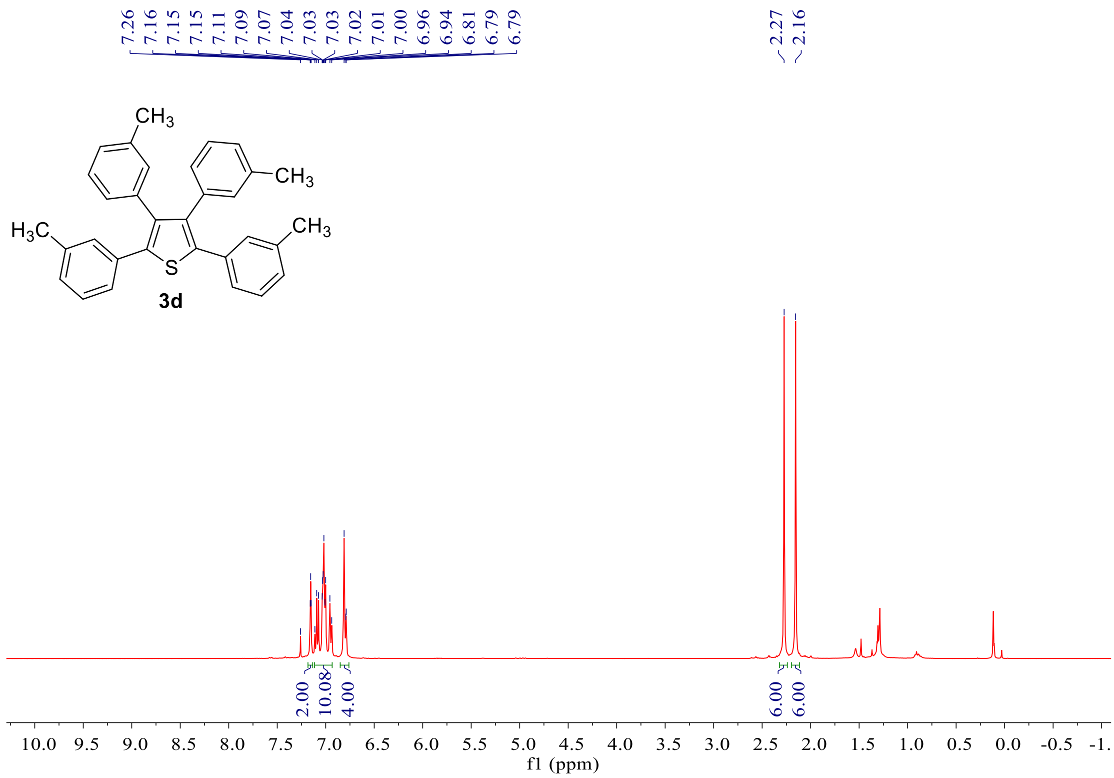
131.77
130.83
129.15
129.12
128.68
77.48
77.16
76.84
21.38
21.31
H3C
CH3
H3C
CH3
S
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.25
7.19
7.18
7.17
7.17
7.16
7.15
6.95
6.95
6.93
6.91
6.91
6.90
6.90
6.89
6.88
6.87
6.87
6.86
6.85
6.84
6.84
6.83
6.81
-0.00
F
S
3c
f1 (ppm)


163.53
163.13
161.07
160.67
138.38
137.79
132.50
132.42
132.06
132.02
131.05
130.97
130.03
129.99
115.76
115.55
115.43
115.22
77.48
77.16
76.84
F
S
3c
f1 (ppm)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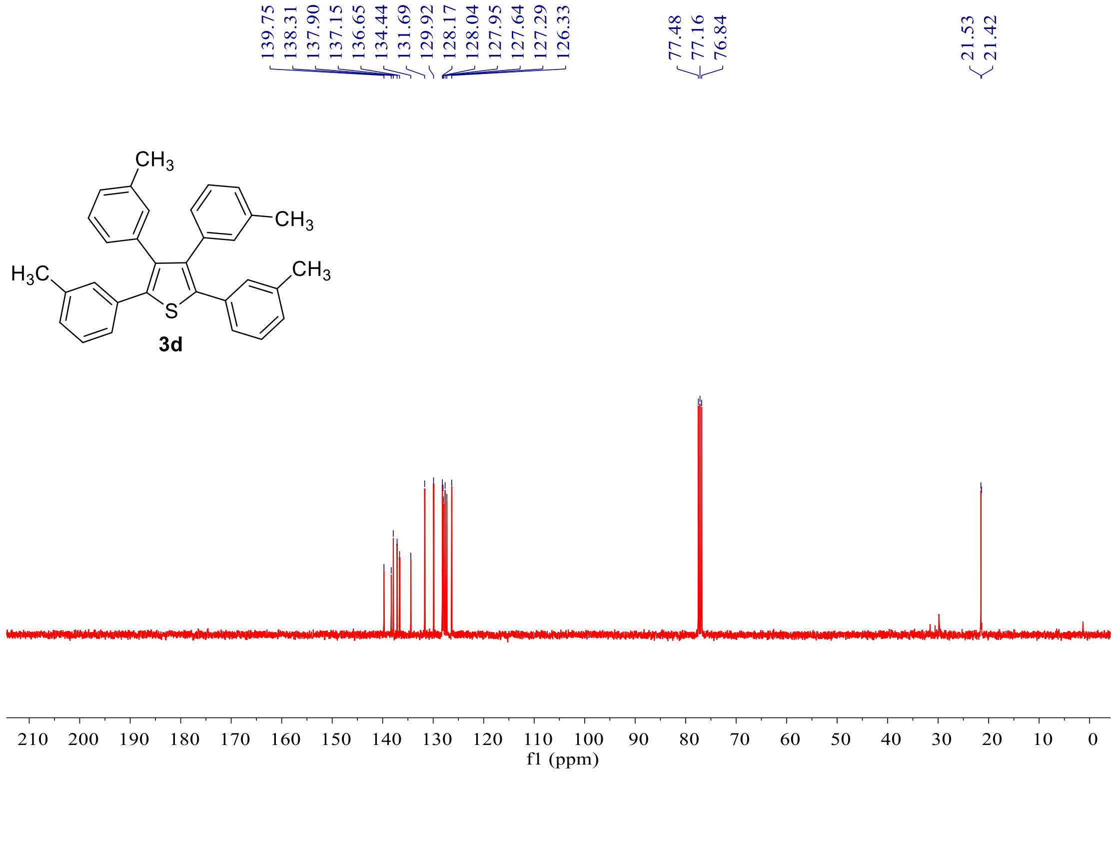
7.16
7.15
7.15
7.11
7.09
7.07
7.04
7.03
7.03
7.02
7.01
7.00
6.96
6.94
6.81
6.79
6.79
2.27
2.16
CH3
CH3
H3C
CH3
S
3d
2.00
10.08
4.00
6.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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137.15
136.65
134.44
131.69
129.92
128.17
128.04
127.95
127.64
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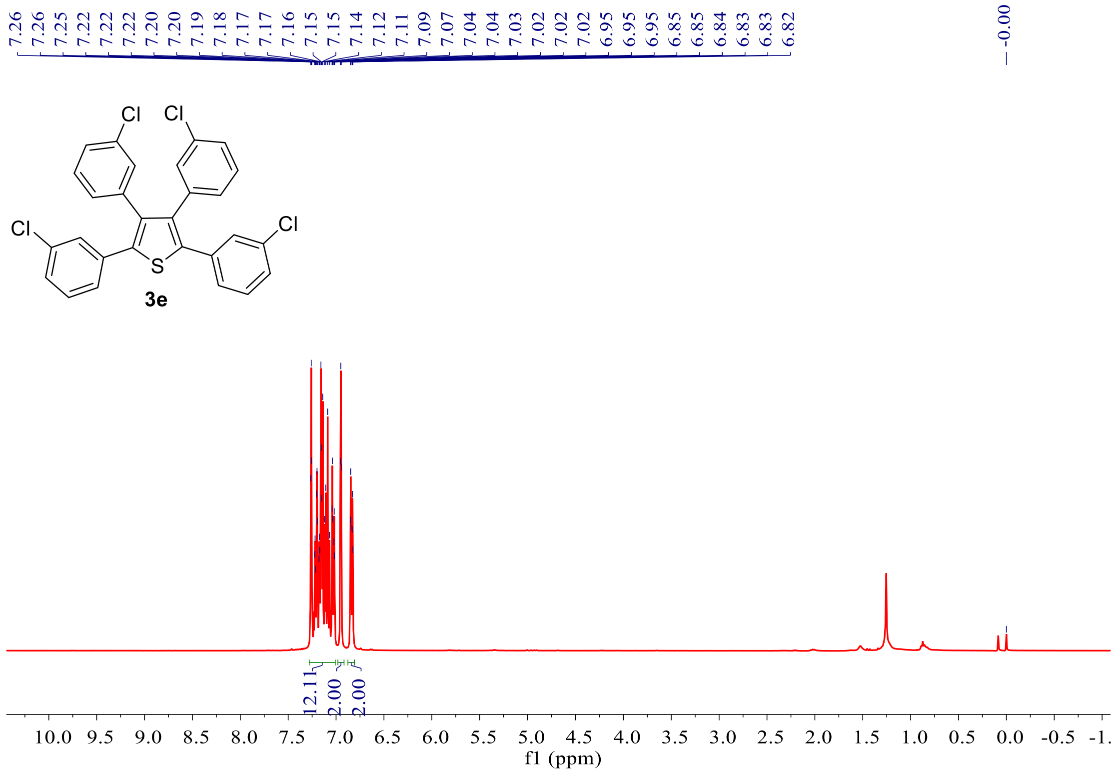
126.33
77.48
77.16
76.84
21.53
21.42
CH3
CH3
H3C
CH3
S
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
7.26
7.25
7.22
7.22
7.22
7.20
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.12
7.11
7.09
7.07
7.04
7.04
7.03
7.02
7.02
7.02
6.95
6.95
6.95
6.85
6.85
6.84
6.83
6.83
6.82
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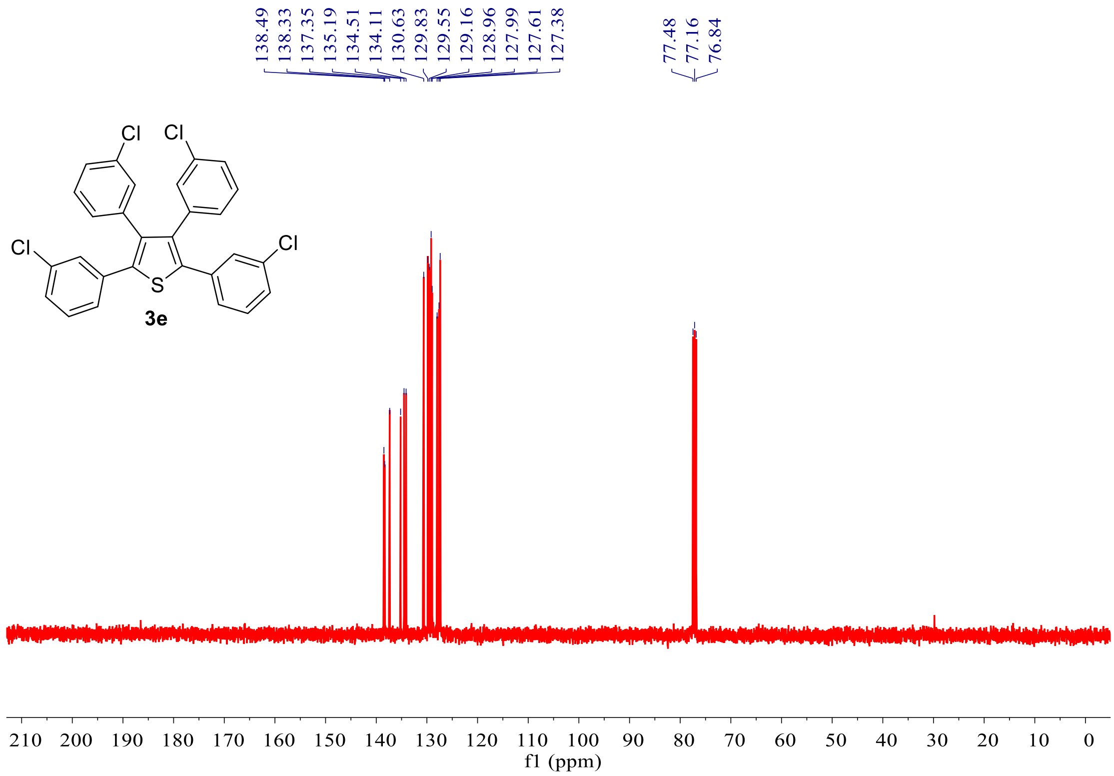
Cl
Cl
Cl
Cl
S
3e
12.11
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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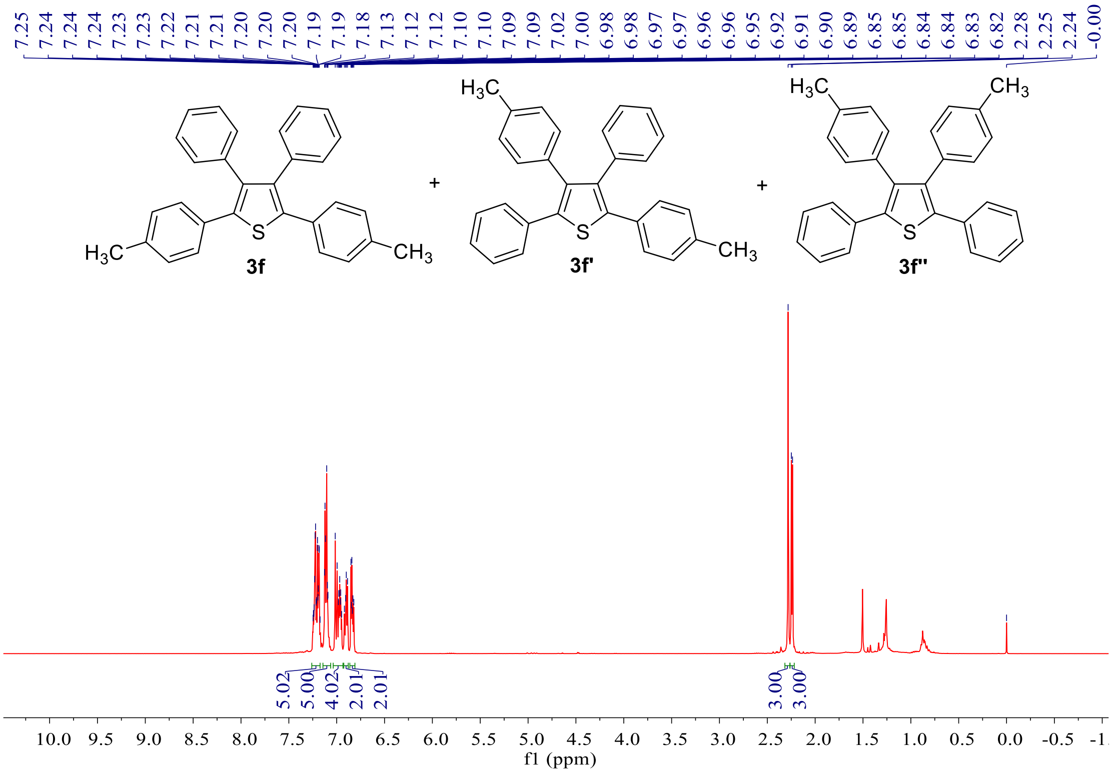
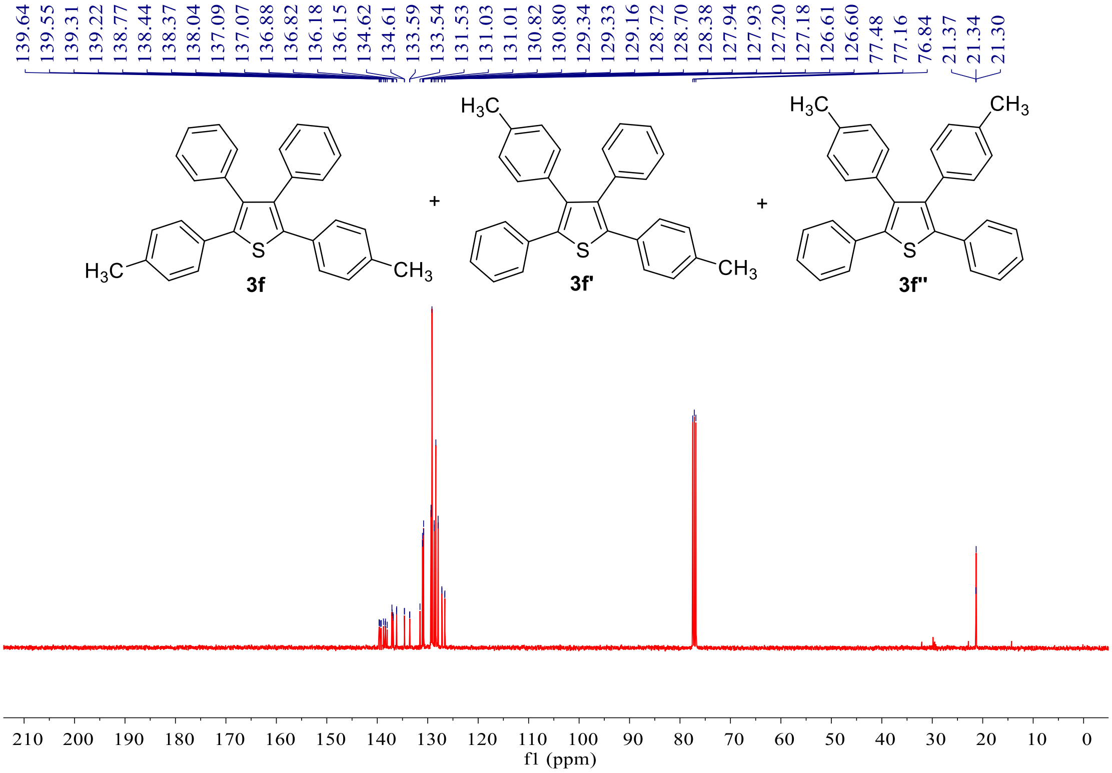
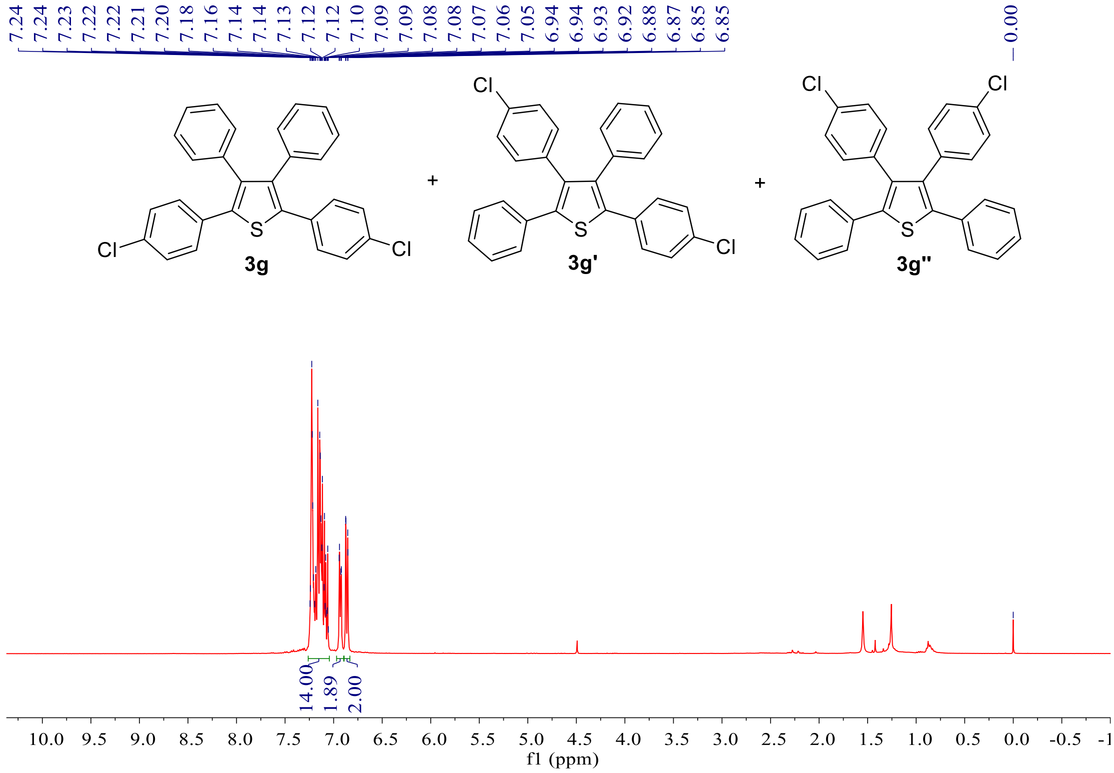
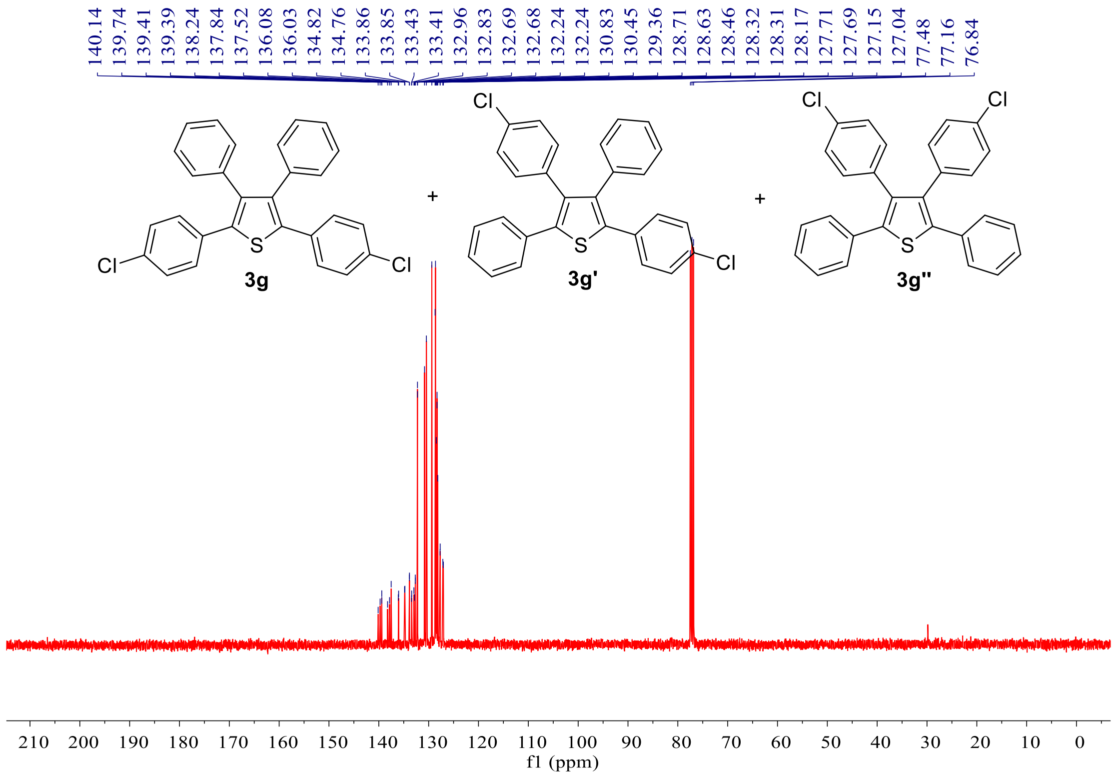
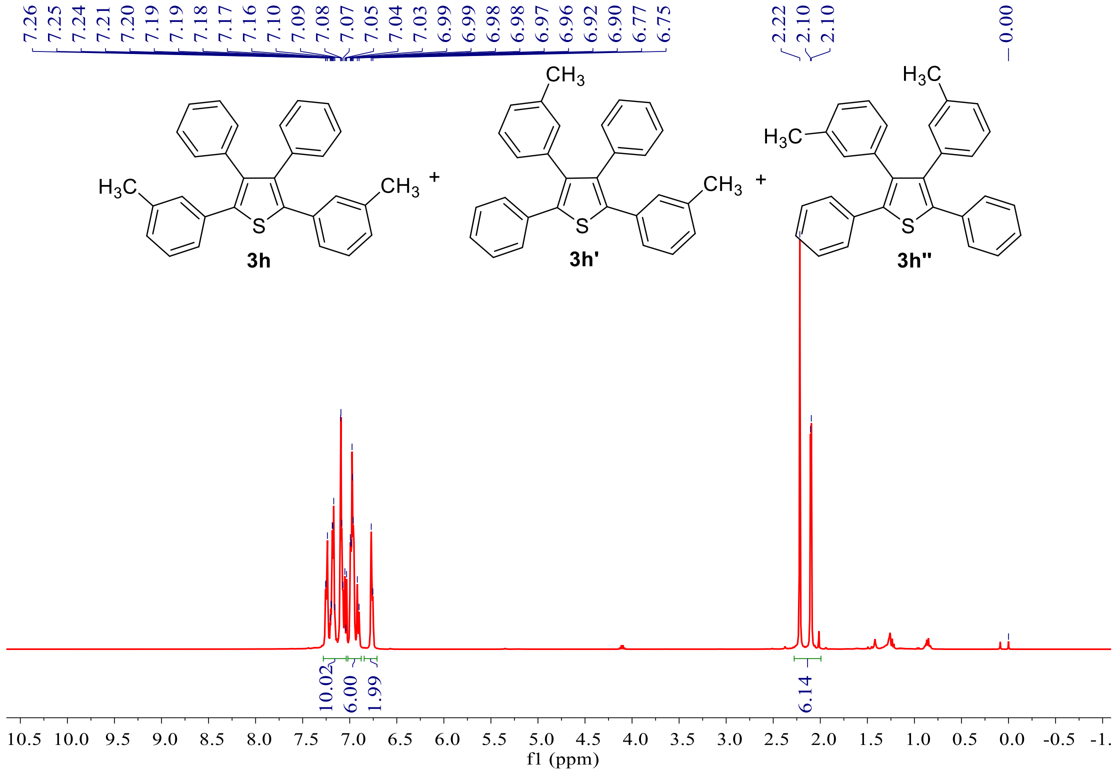
134.51
134.11
130.63
129.83
129.55
129.16
128.96
127.99
127.61
127.38
77.48
77.16
76.84
Cl
Cl
Cl
Cl
S
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3f
3f'
3f''
f1 (ppm)


3f
3f'
3f''
f1 (ppm)


7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.18 7.16 7.14 7.14 7.13 7.12 7.12 7.10 7.09 7.09 7.08 7.08 7.07 7.06 7.05 6.94 6.94 6.93 6.92 6.88 6.87 6.85 6.85
0.00
Cl
S
3g
3g'
3g''
+
14.00
1.89
2.00
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 0.0 -0.5 -1
f1 (ppm)


140.14 139.74 139.41 139.39 138.24 137.84 137.52 136.08 136.03 134.82 134.76 133.86 133.85 133.43 133.41 132.96 132.83 132.69 132.68 132.24 132.24 130.83 130.45 129.36 128.71 128.63 128.46 128.32 128.31 128.17 127.71 127.69 127.15 127.04 77.48 77.16 76.84
Cl
S
3g
3g'
3g''
+
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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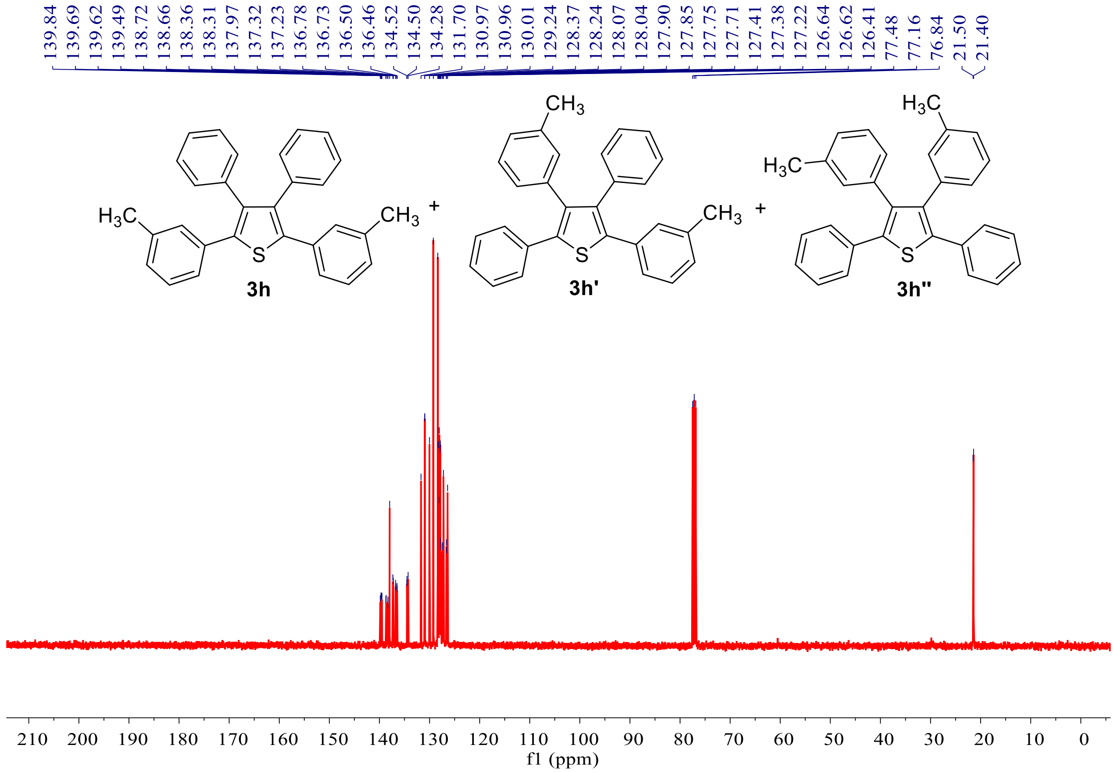
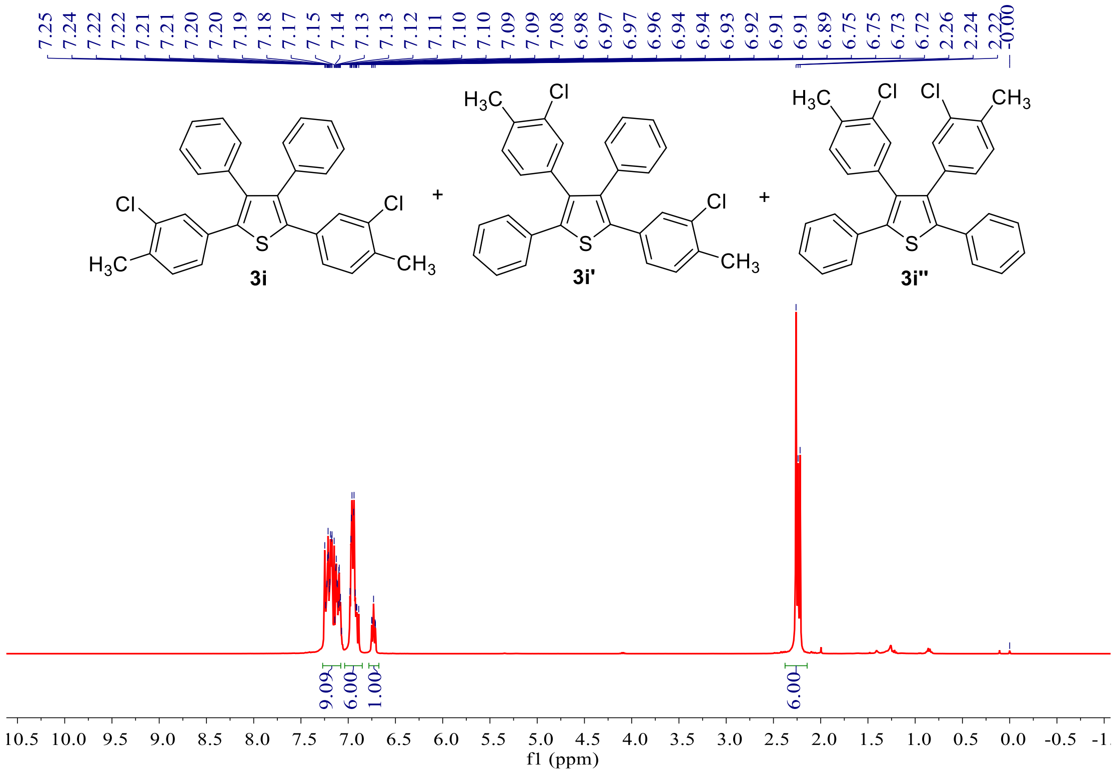
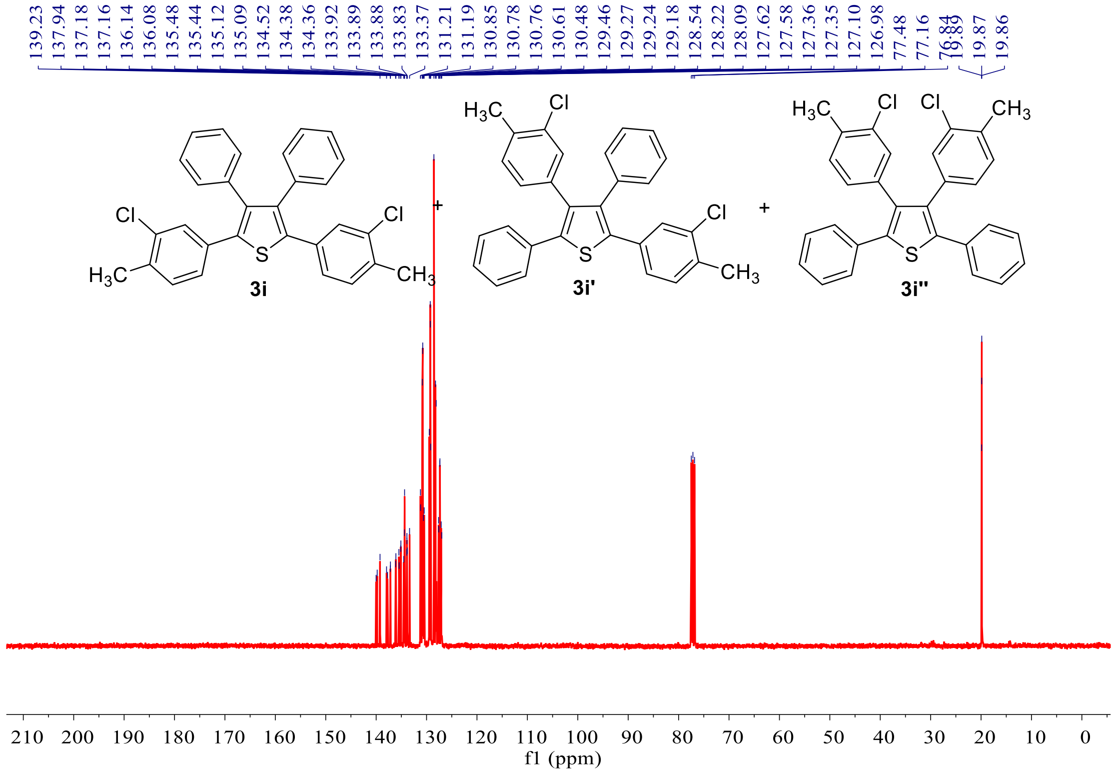
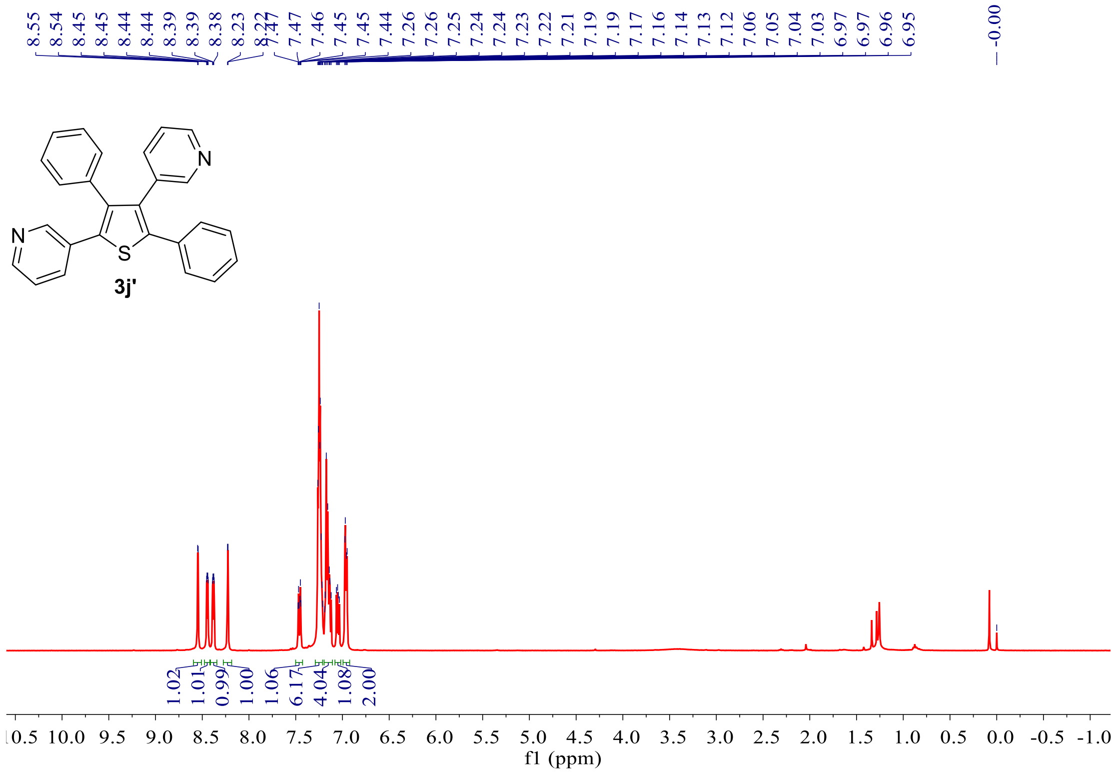
2.22 2.10 2.10
0.00
3h
3h'
3h''
10.02
6.00
1.99
6.14
f1 (ppm)


139.84 139.69 139.62 139.49 138.72 138.66 138.36 138.31 137.97 137.32 137.23 136.78 136.73 136.50 136.46 134.52 134.50 134.28 131.70 130.97 130.96 130.01 129.24 128.37 128.24 128.07 128.04 127.90 127.85 127.75 127.71 127.41 127.38 127.22 126.64 126.62 126.41 77.48 77.16 76.84
21.50 21.40
3h
3h'
3h''
f1 (ppm)



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-0.00
N
N
S
3j'
1.02 1.01 0.99 1.00 1.06 6.17 4.04 1.08 2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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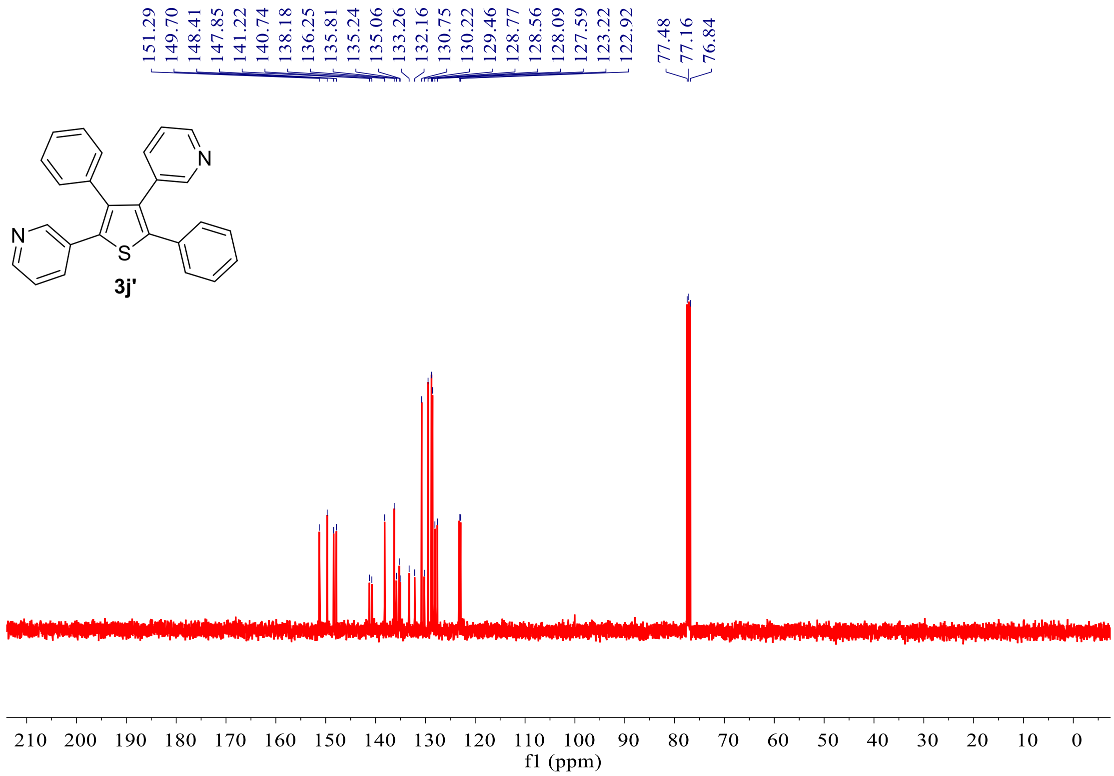
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S
3j'
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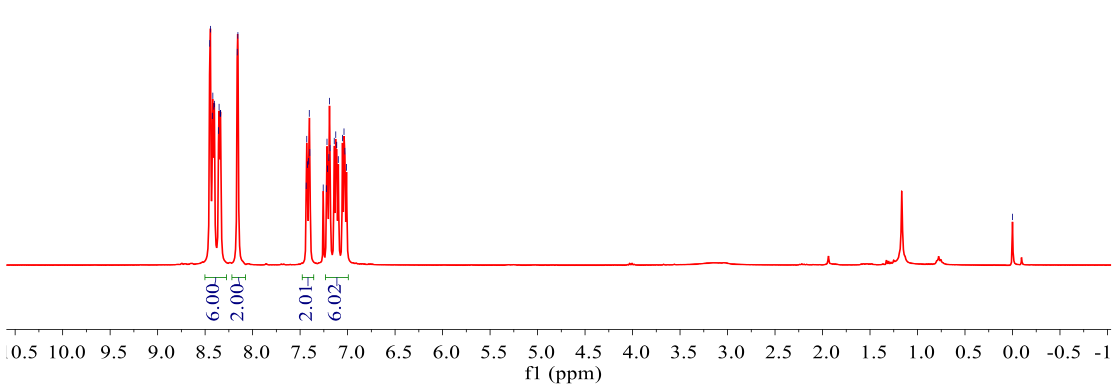
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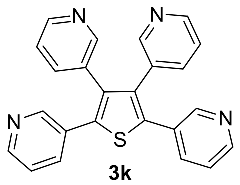
0.00
6.00 2.00 2.01 6.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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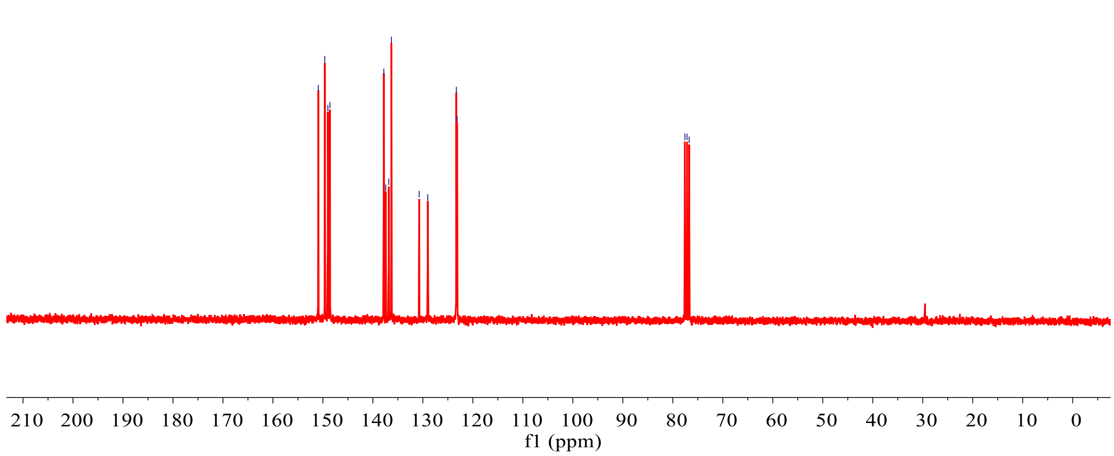
S

3k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77.59 77.16 76.74
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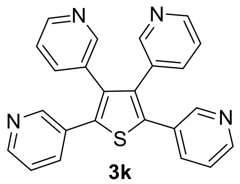
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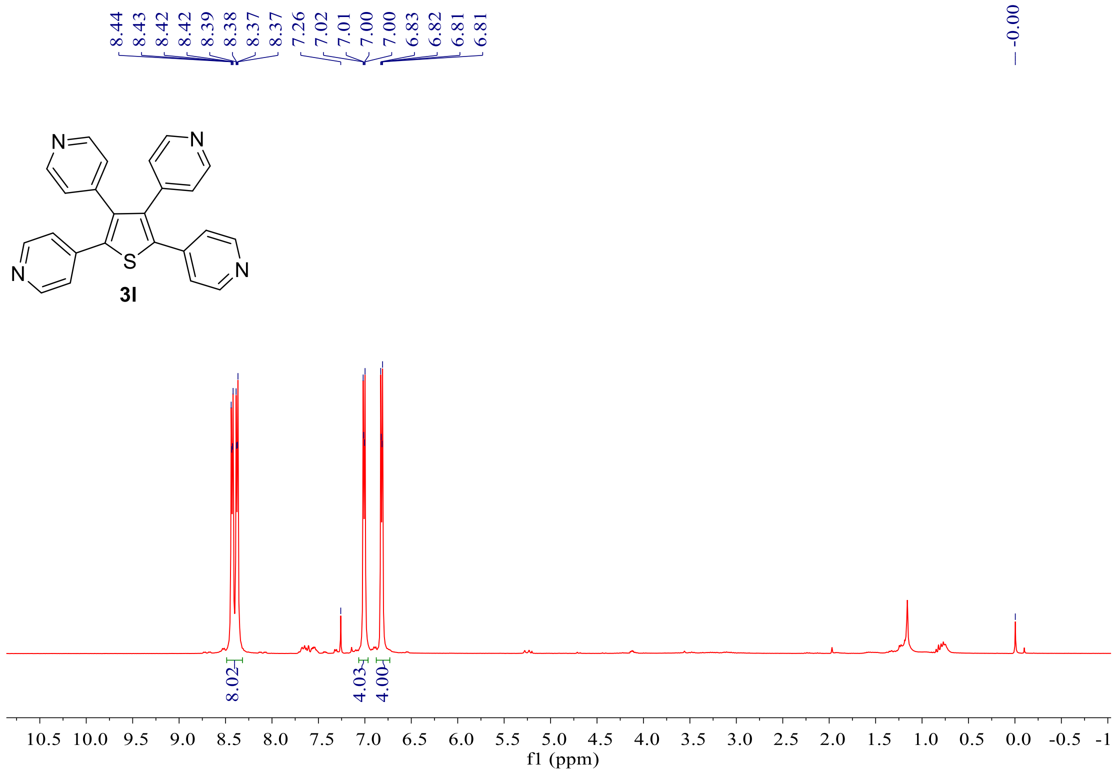
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7.00
6.83
6.82
6.81
6.81
-0.00
3l
8.02
4.03
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
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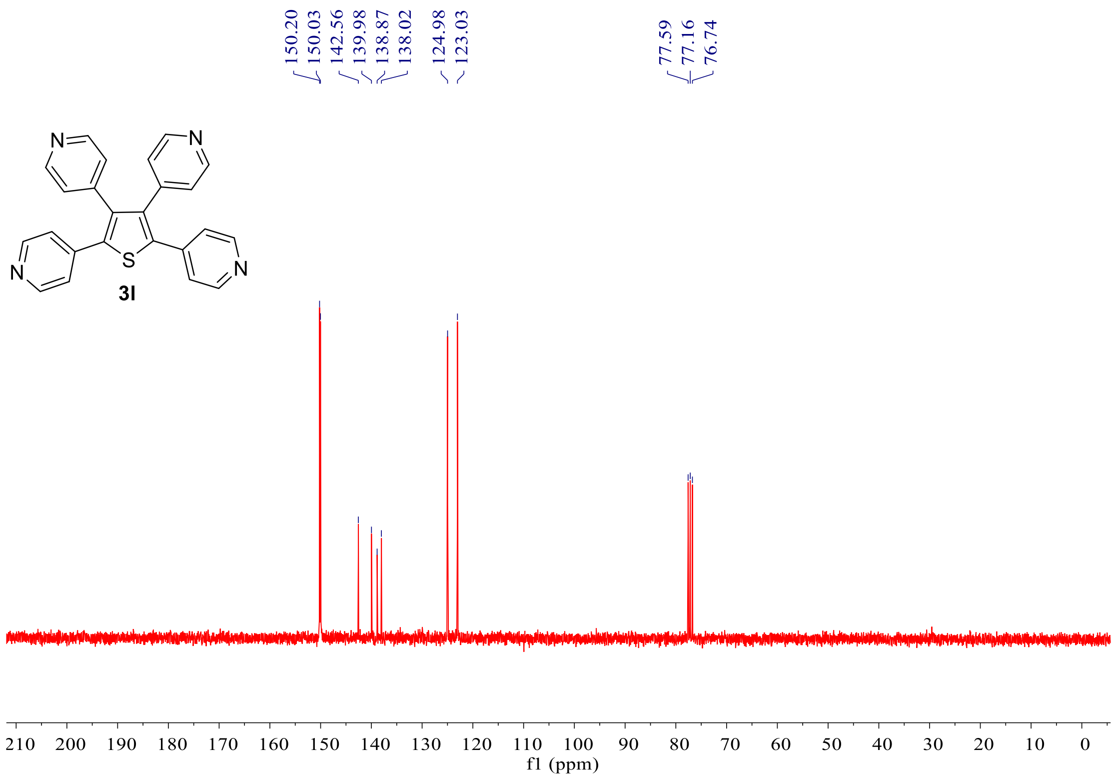
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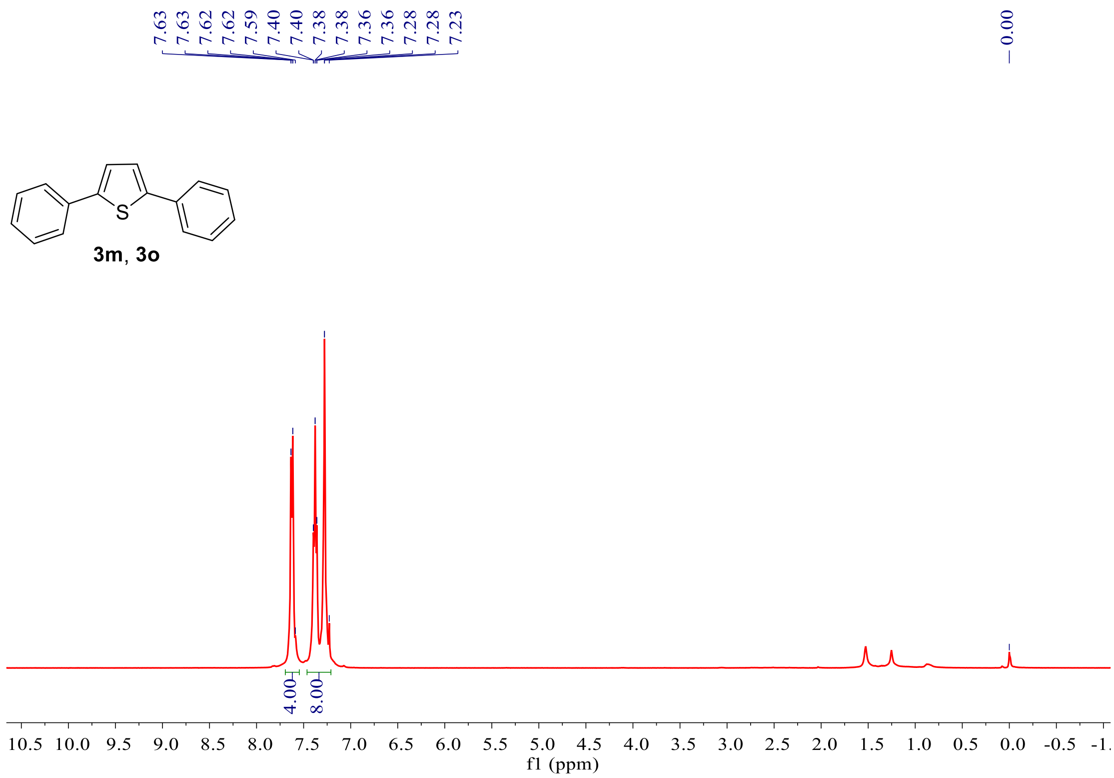
f1 (ppm)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7.62
7.62
7.59
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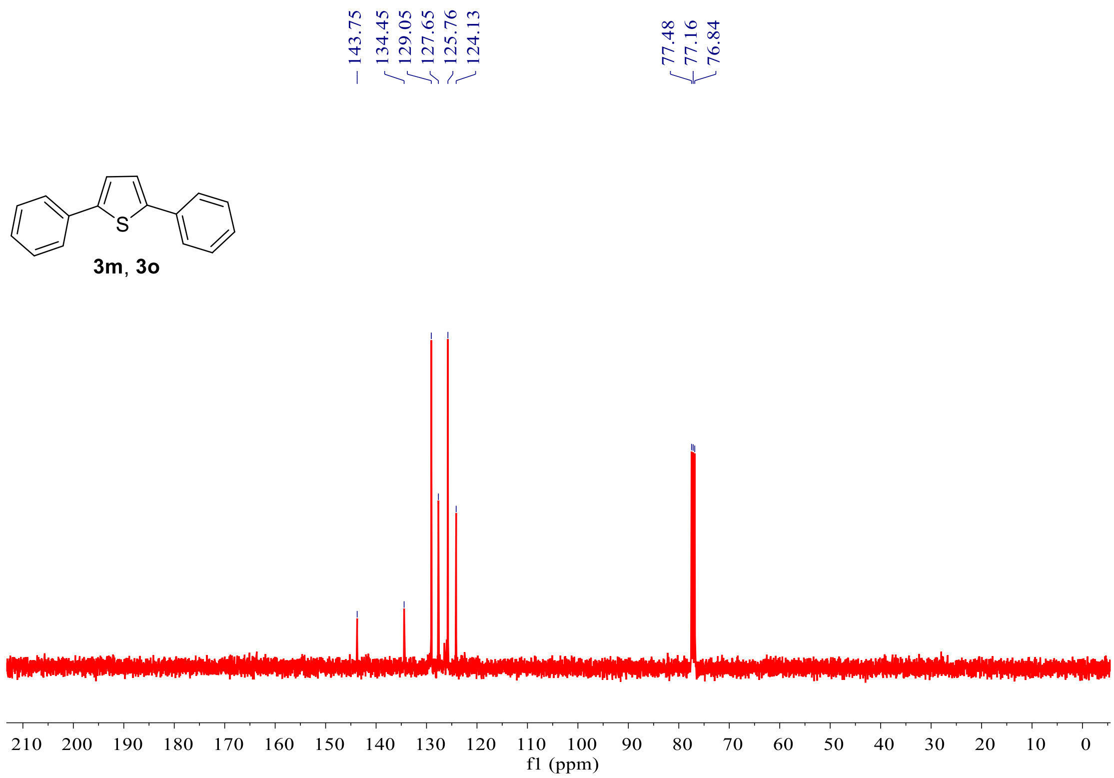
7.40
7.38
7.38
7.36
7.36
7.28
7.28
7.23
0.00
S
3m, 3o
4.00
8.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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127.65
125.76
124.13
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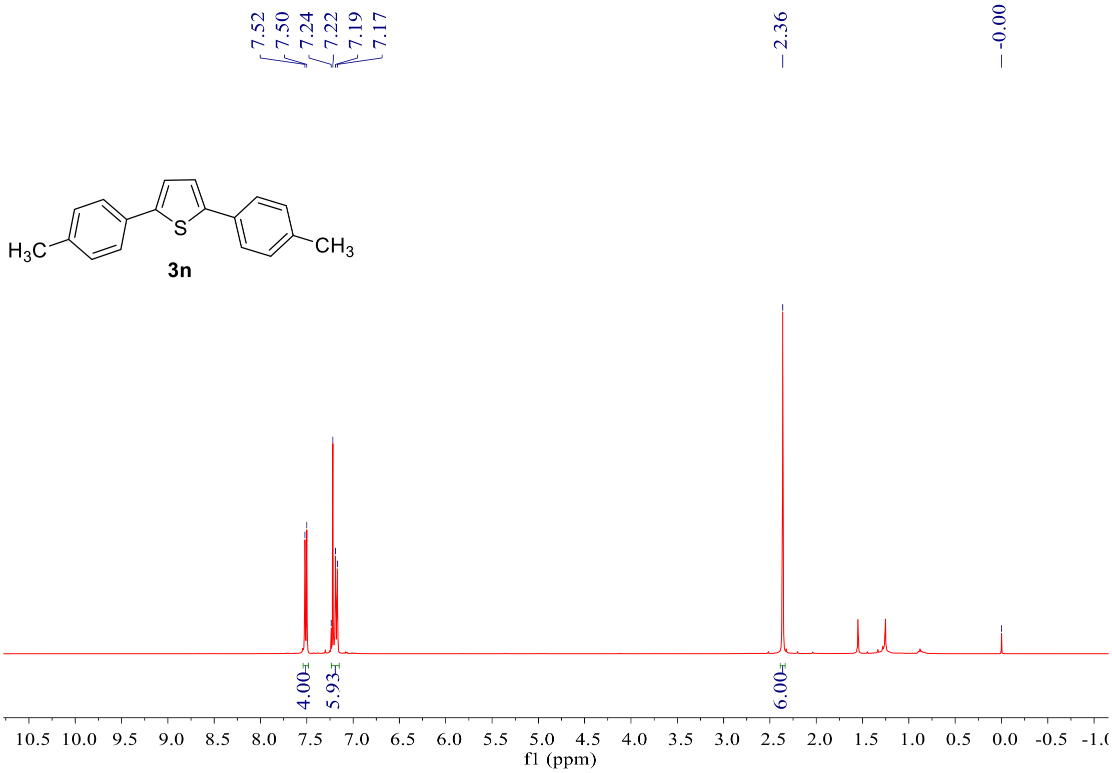
77.16
76.84
S
3m, 3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.50
7.24
7.22
7.19
7.17
2.36
-0.00
H3C
S
CH3
3n
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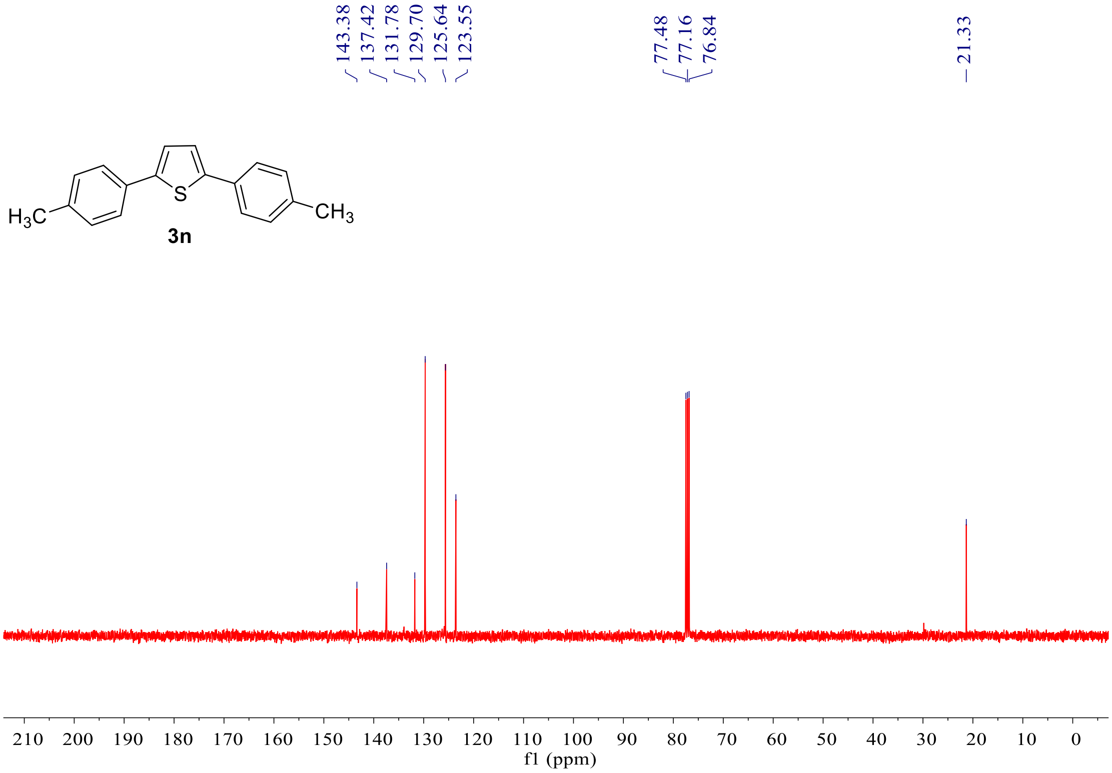
5.93
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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H3C
S
CH3
3n
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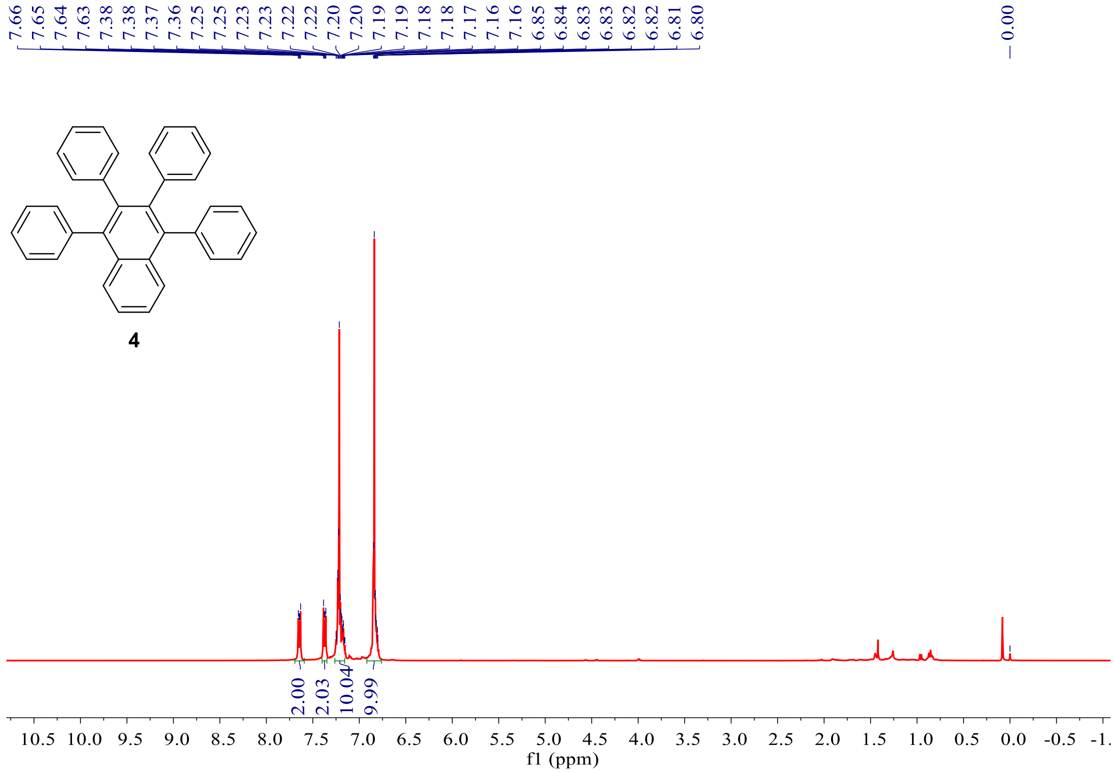
f1 (ppm)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7.63
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7.38
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7.36
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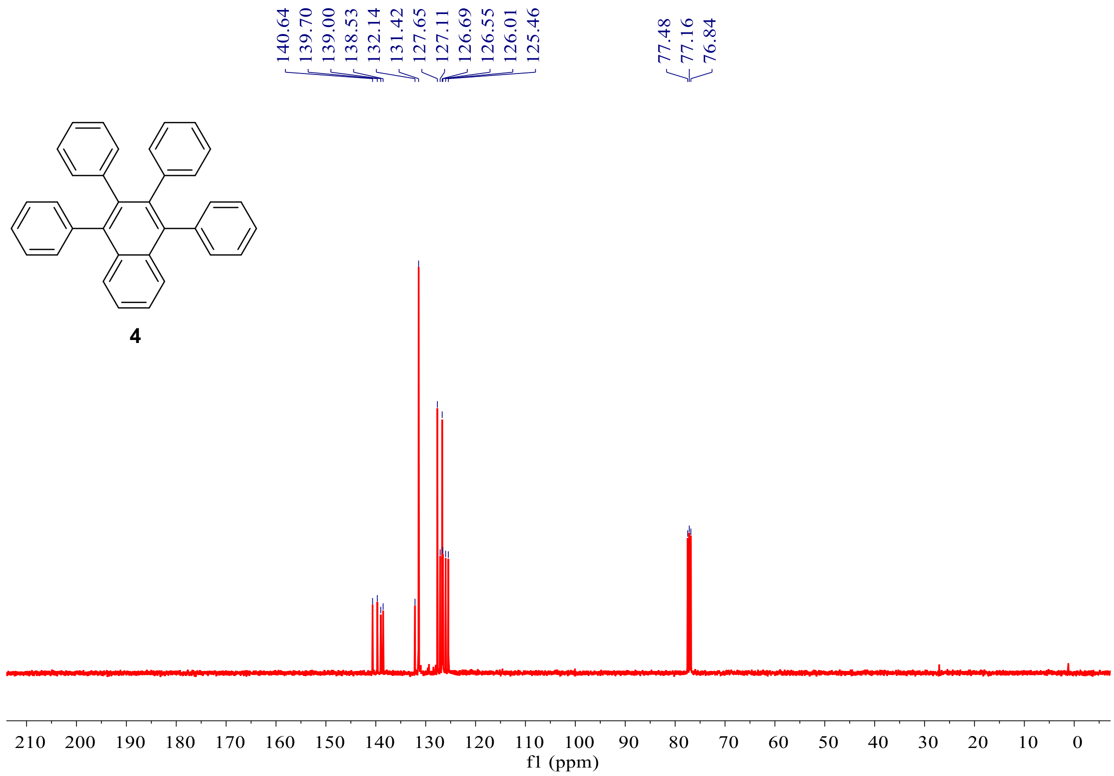
7.25
7.23
7.23
7.22
7.22
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.16
6.85
6.84
6.83
6.83
6.82
6.82
6.81
6.80
0.00
4
2.00
2.03
10.04
9.99
f1 (ppm)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132.14
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126.55
126.01
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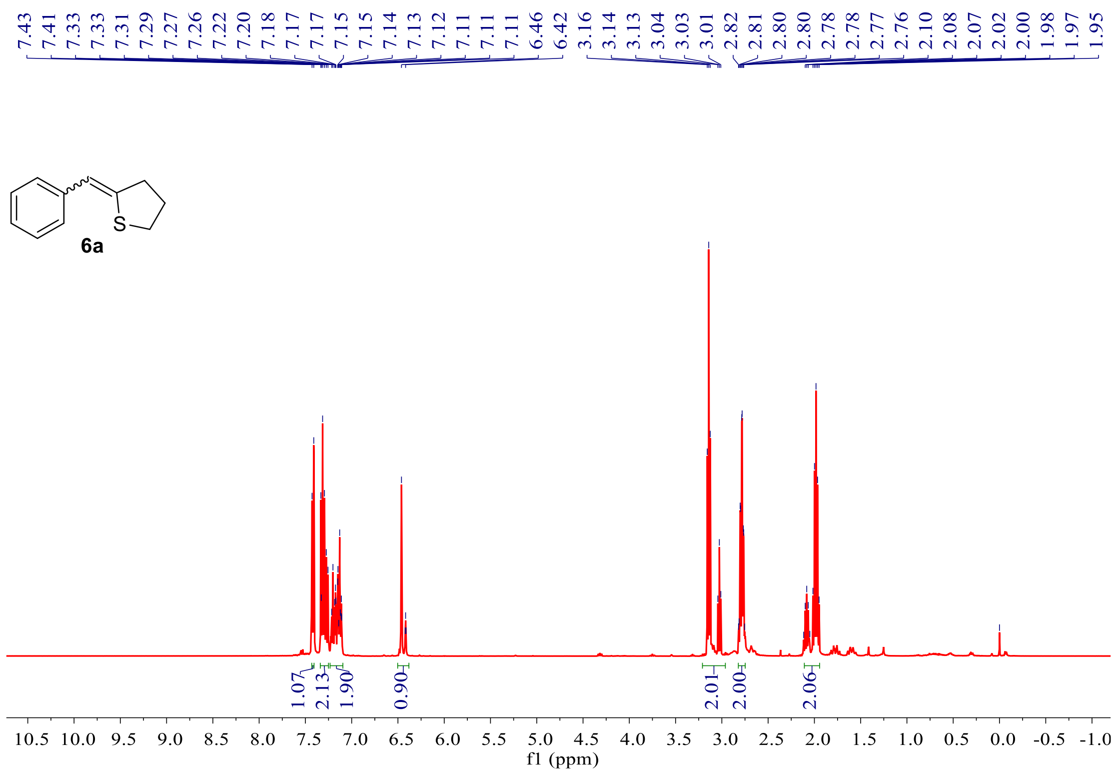
76.84
4
f1 (ppm)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S
6a
1.07 2.13 1.90 0.90 2.01 2.00 2.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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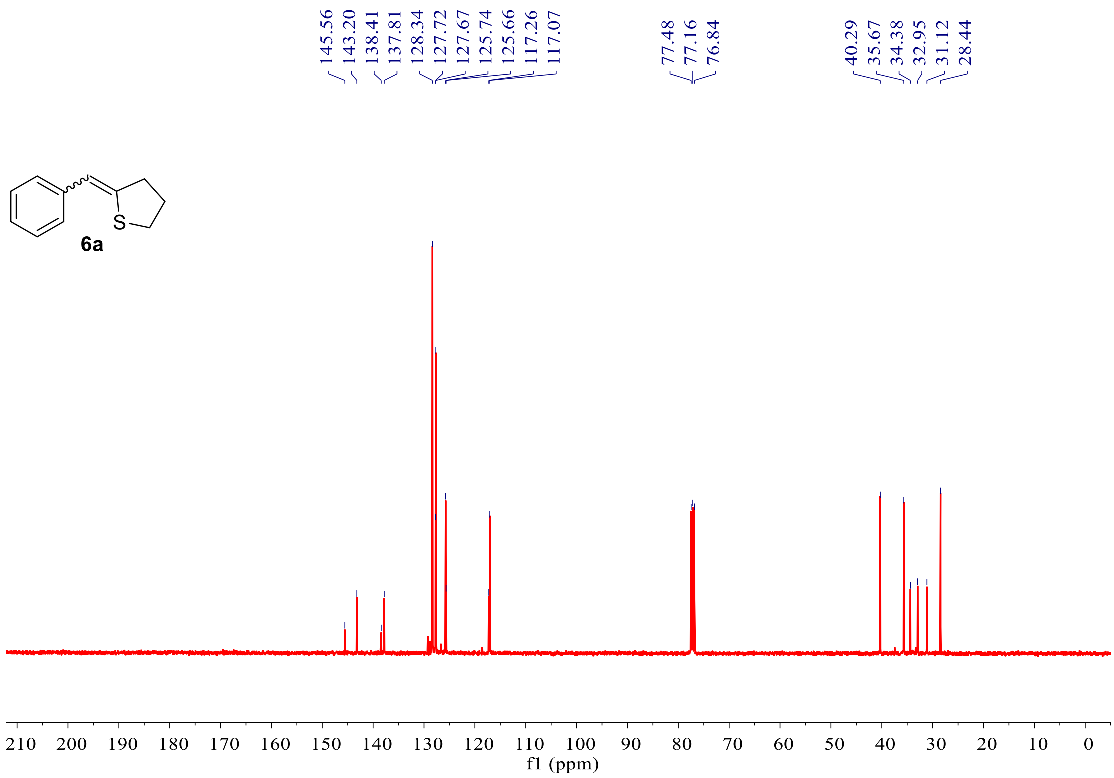
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77.48 77.16 76.84
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S
6a
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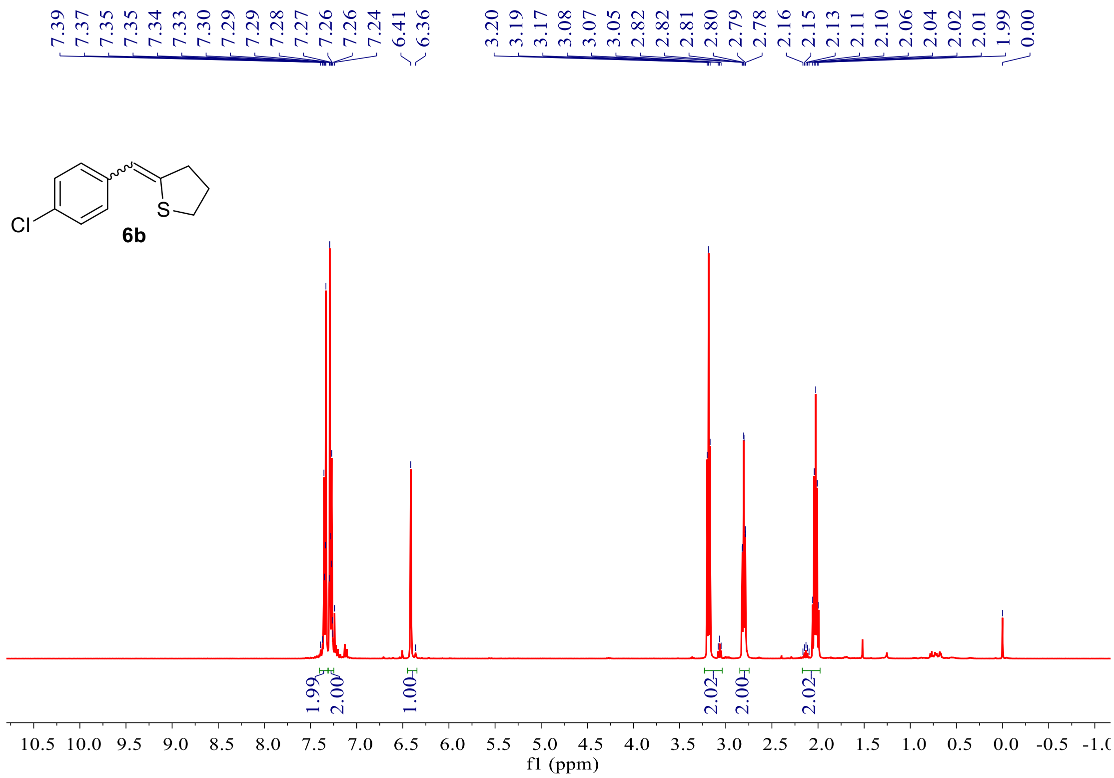
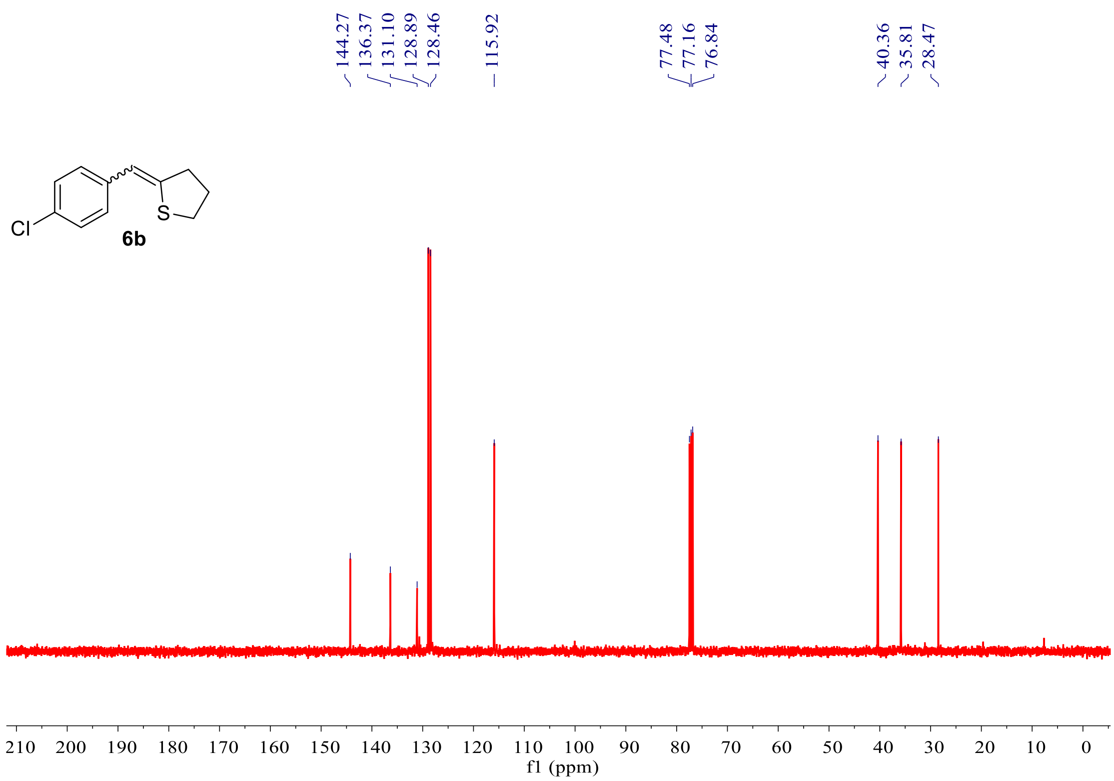
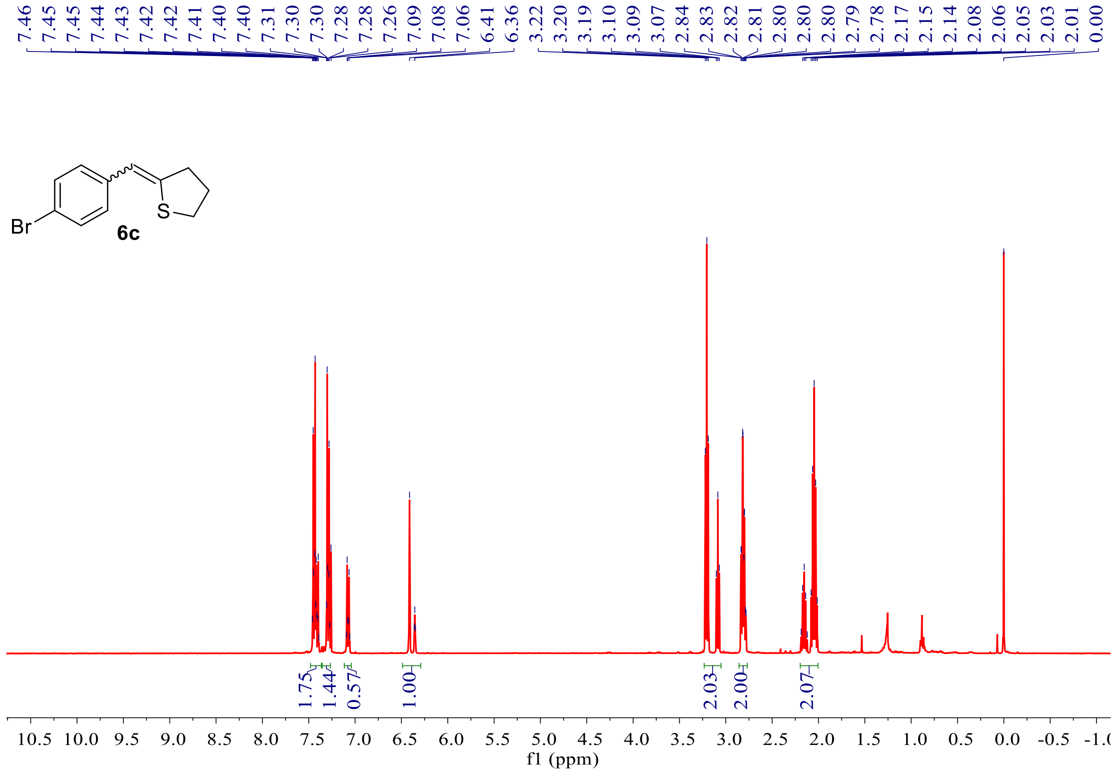
f1 (ppm)



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S
6c
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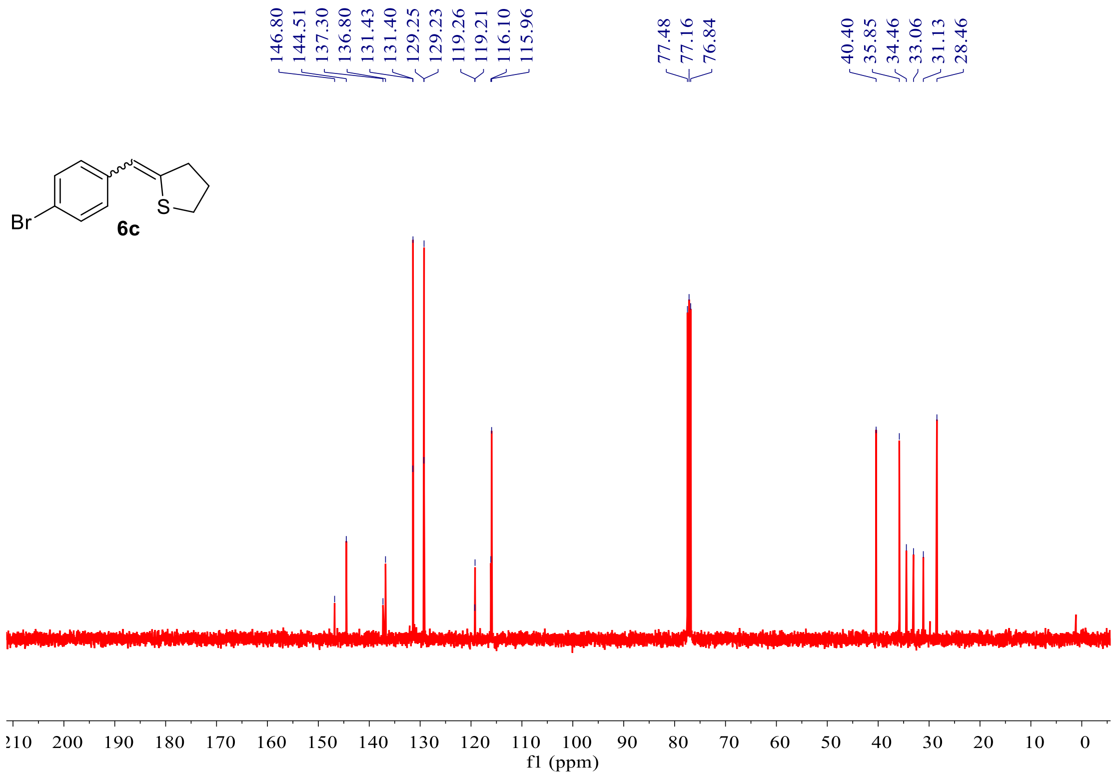
f1 (ppm)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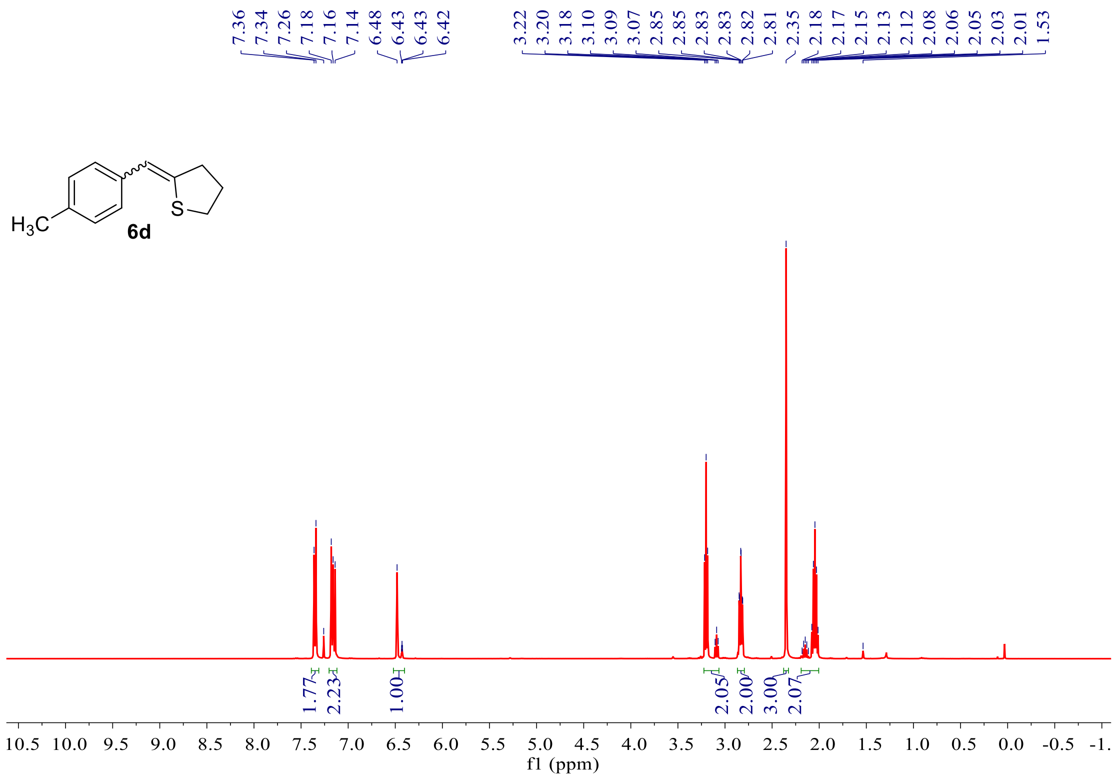
Br
S
6c
f1 (ppm)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3.22 3.20 3.18 3.10 3.09 3.07 2.85 2.85 2.83 2.83 2.82 2.81 2.35 2.18 2.17 2.15 2.13 2.12 2.08 2.06 2.05 2.03 2.01 1.53
H_3C
S
6d
1.77 2.23 1.00 2.05 2.00 3.00 2.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
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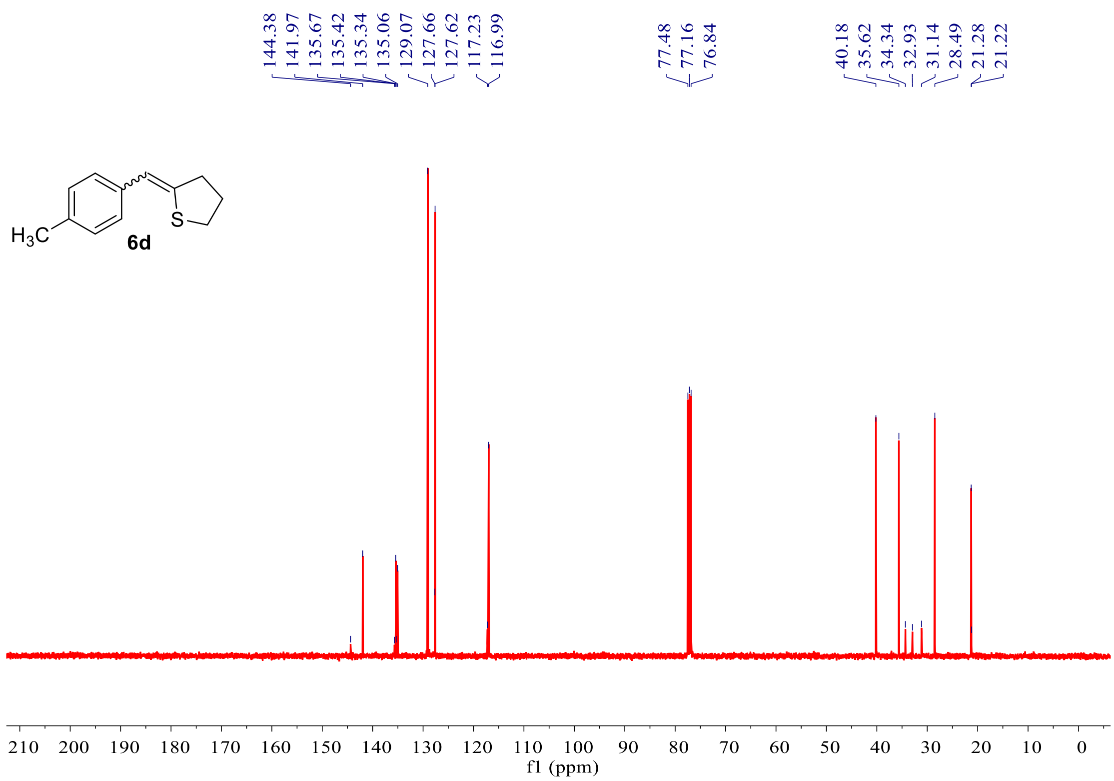
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H_3C
S
6d
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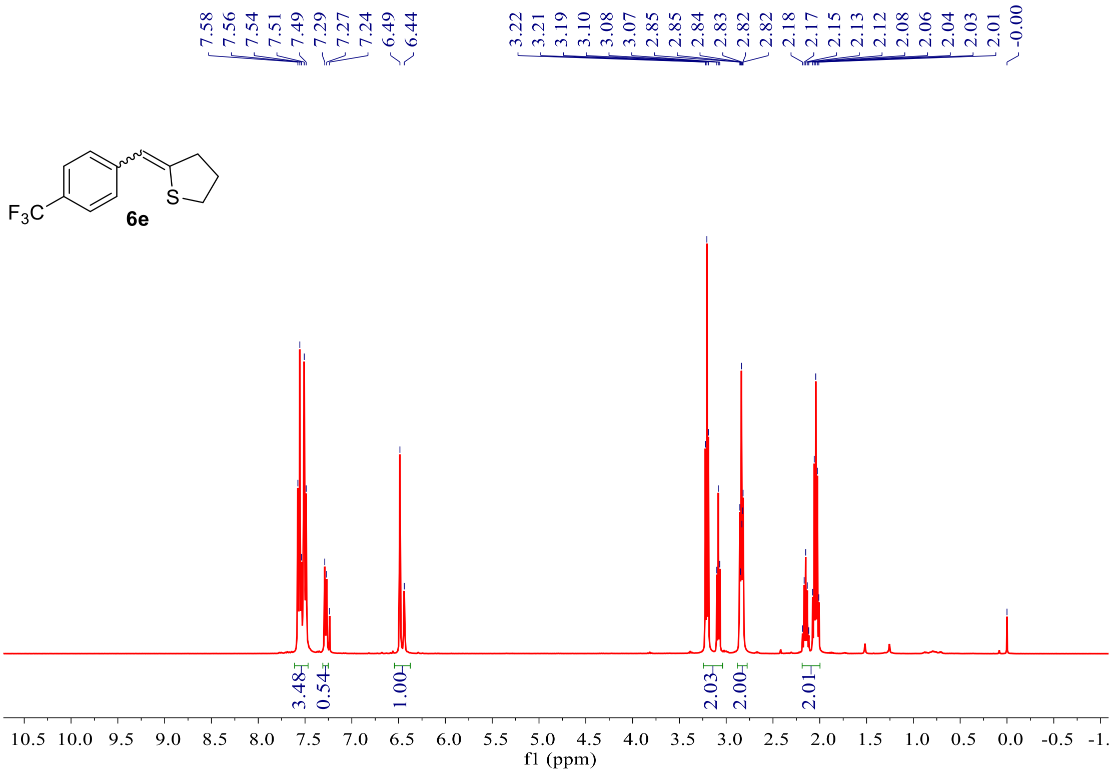
f1 (ppm)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F3C
S
6e
3.48 0.54 1.00 2.03 2.00 2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
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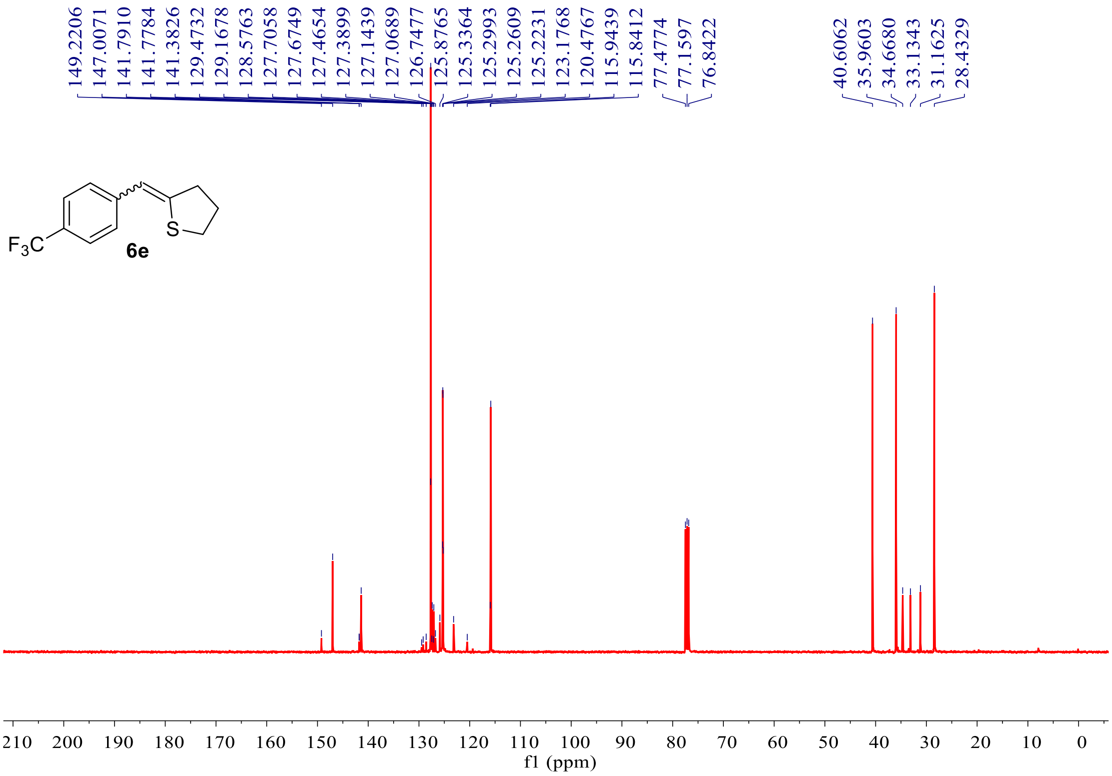
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77.4774 77.1597 76.8422
40.6062 35.9603 34.6680 33.1343 31.1625 28.4329
F3C
S
6e
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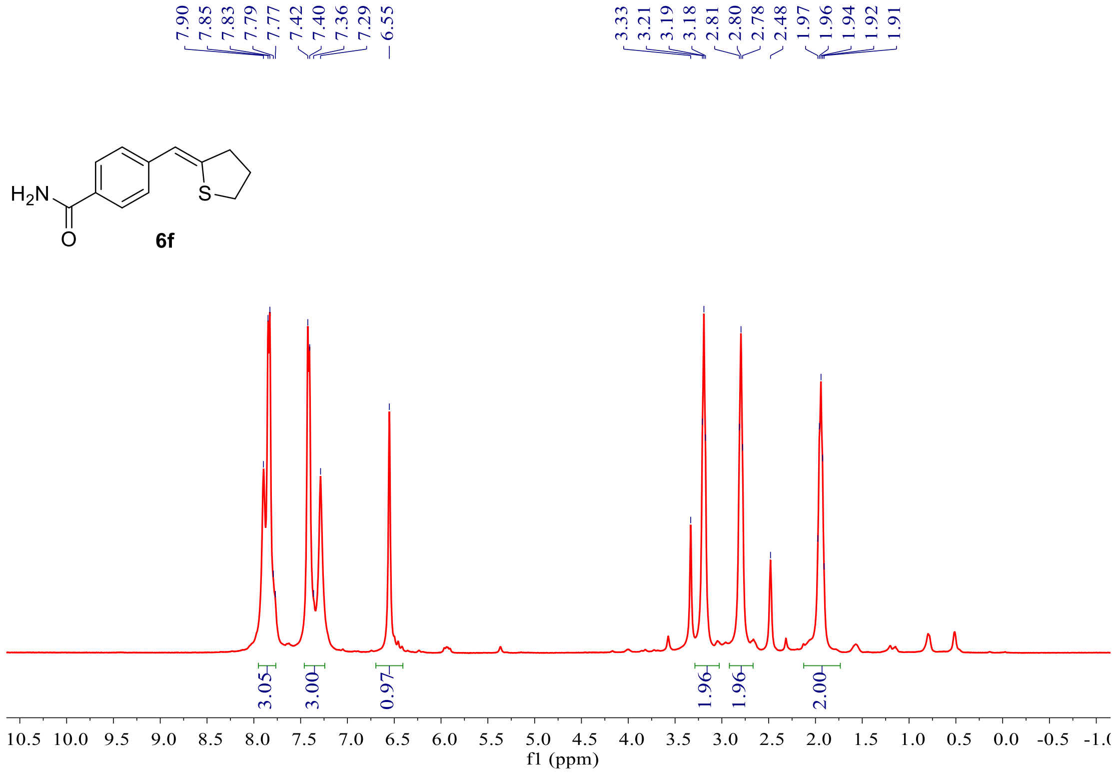
f1 (ppm)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2.78
2.48
1.97
1.96
1.94
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O
S
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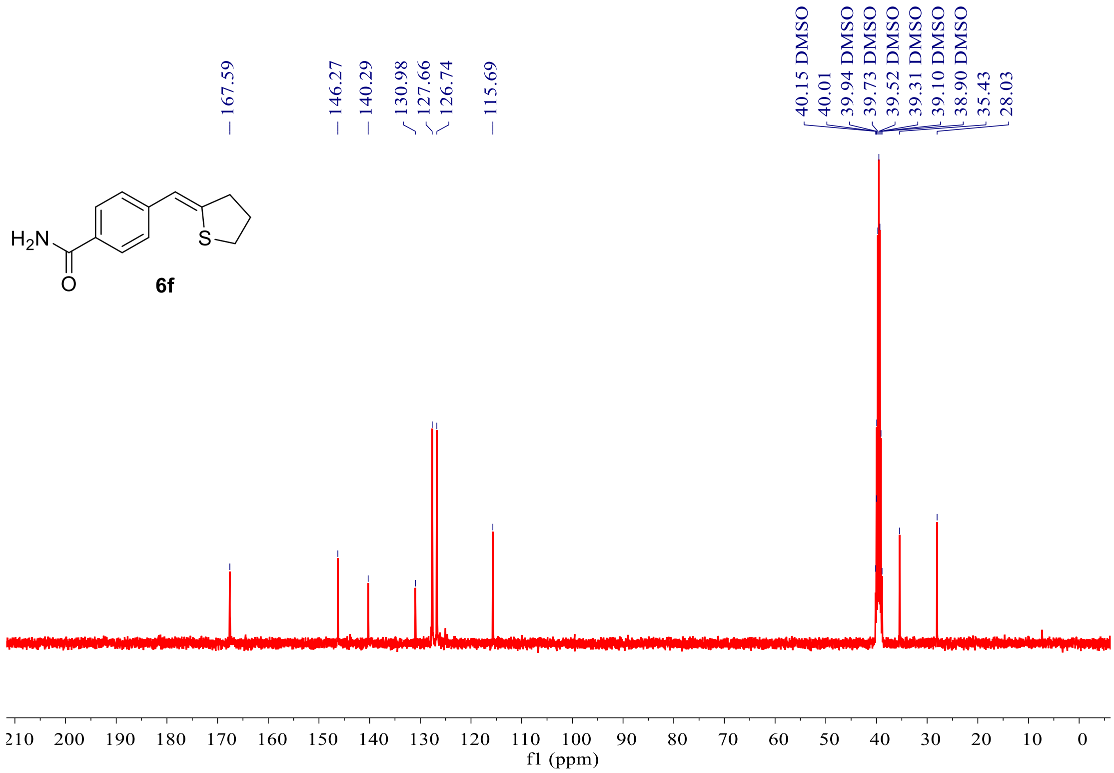
1.96
1.96
2.00
f1 (ppm)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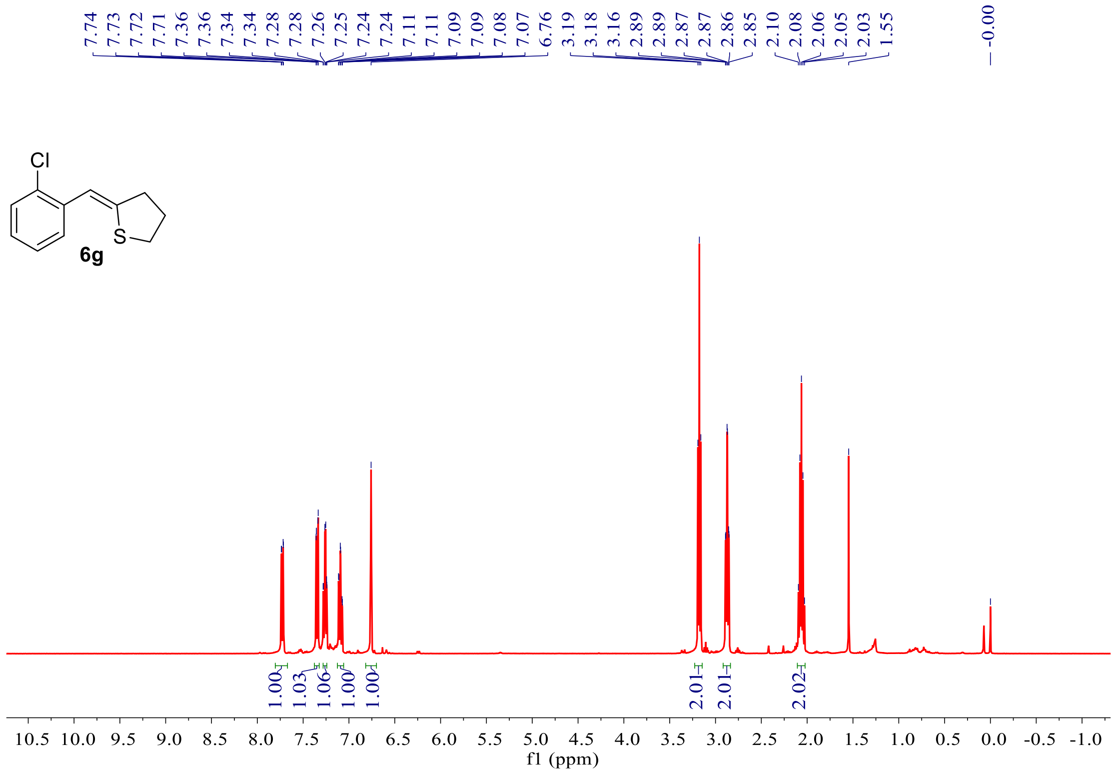
28.03
H2N
O
S
6f
f1 (ppm)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Cl
S
6g
1.00 1.03 1.06 1.00 1.00 2.01 2.01 2.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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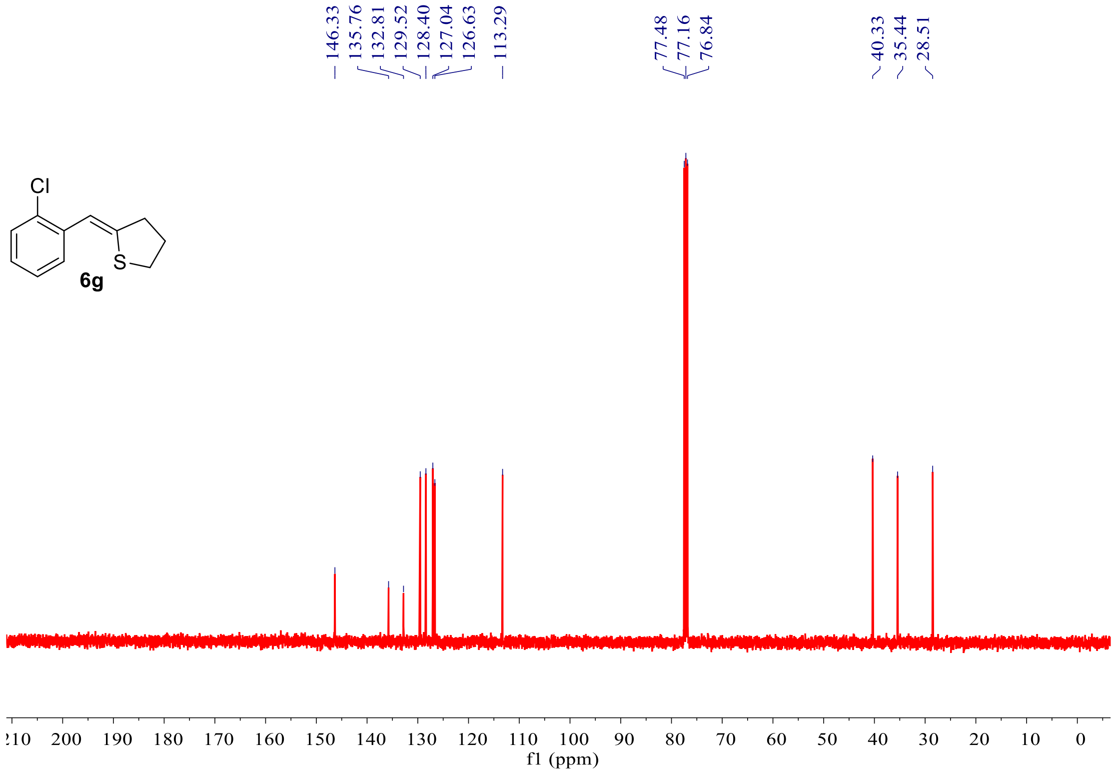
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6g
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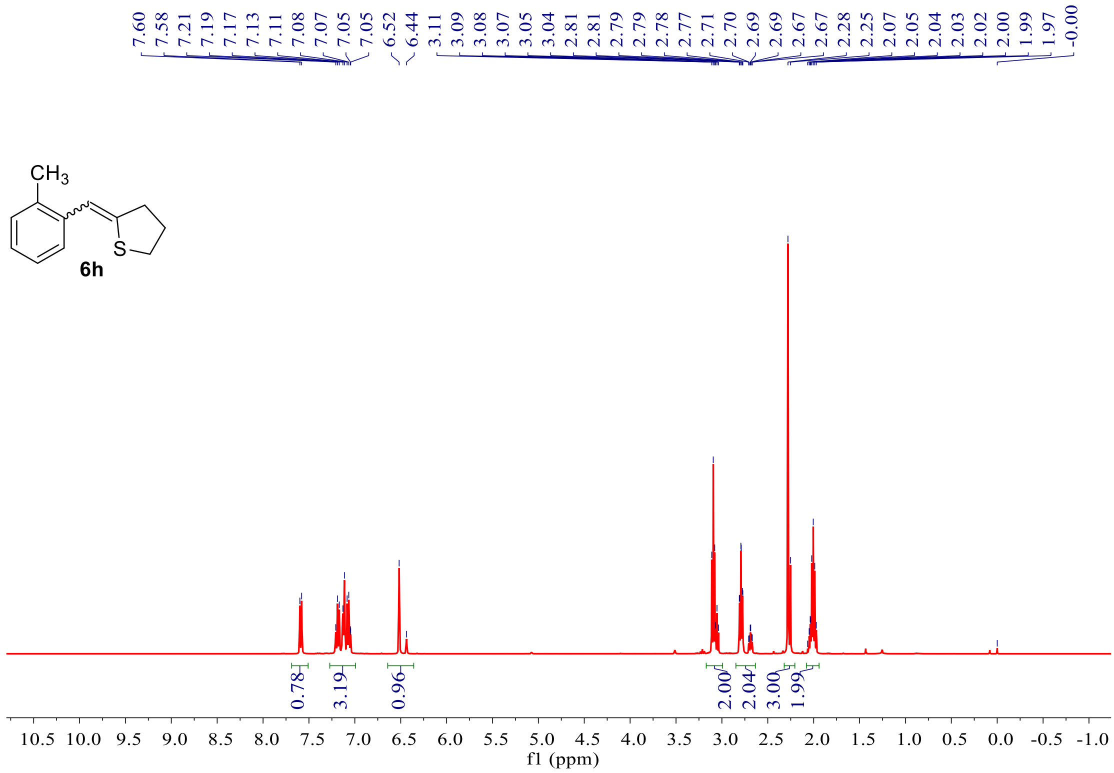
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2.02
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1.99
1.97
-0.00
CH3
S
6h
0.78
3.19
0.96
2.00
2.04
3.00
1.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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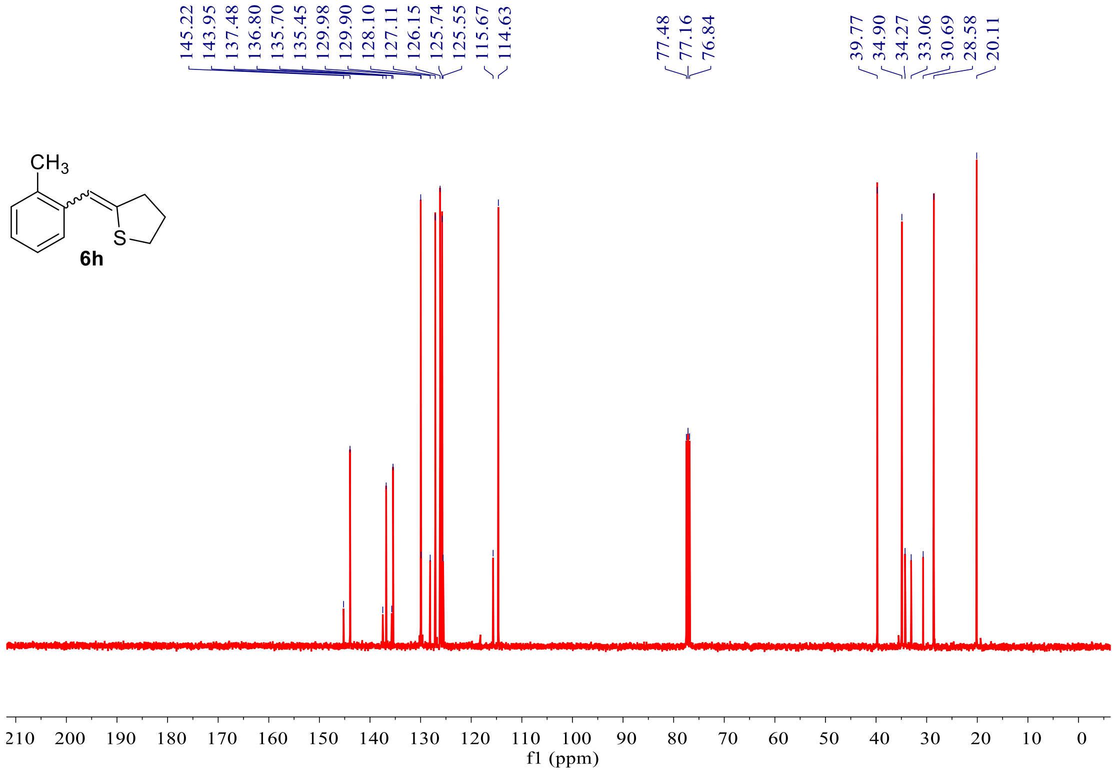
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114.63
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77.16
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34.27
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20.11
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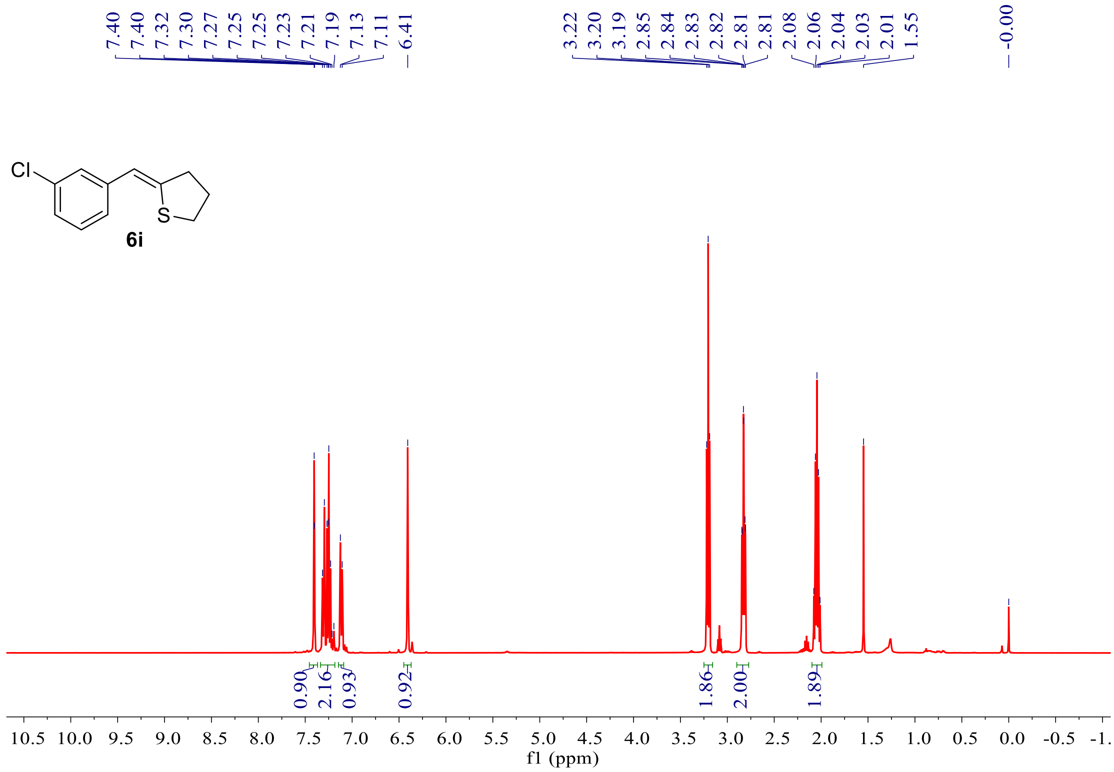
f1 (ppm)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7.23
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7.19
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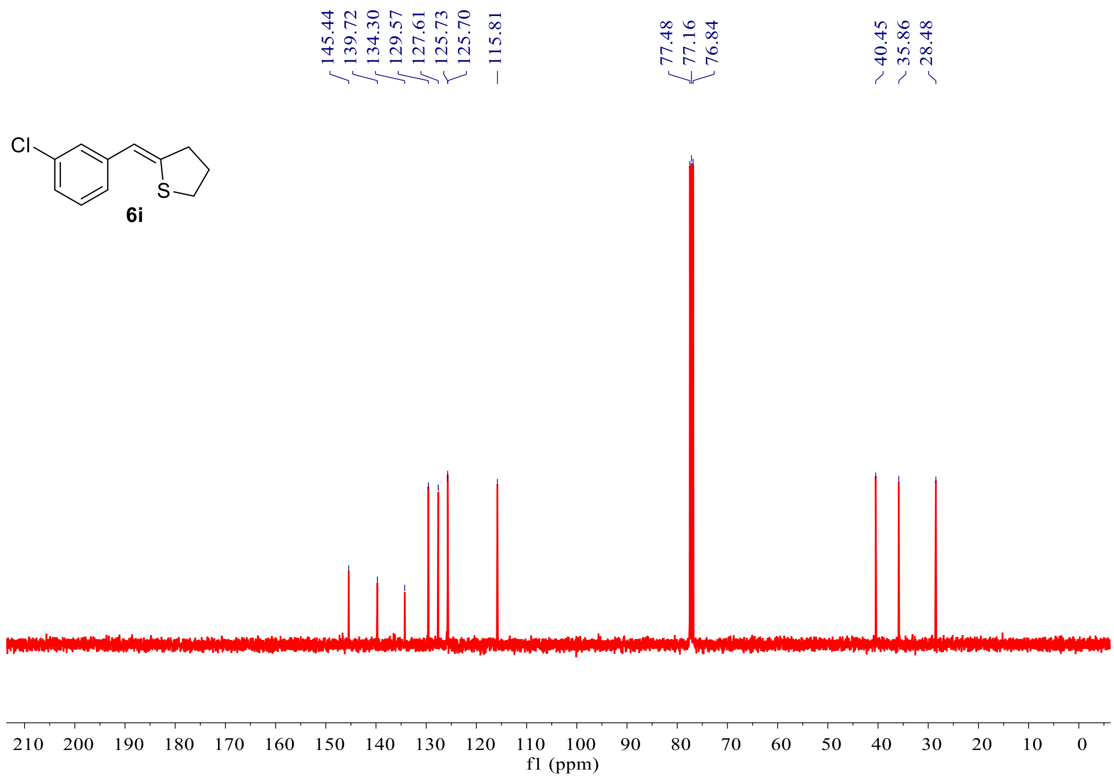
7.11
6.41
3.22
3.20
3.19
2.85
2.84
2.83
2.82
2.81
2.81
2.08
2.06
2.04
2.03
2.01
1.55
-0.00
Cl
S
6i
0.90
2.16
0.93
0.92
1.86
2.00
1.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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115.81
77.48
77.16
76.84
40.45
35.86
28.48
Cl
S
6i
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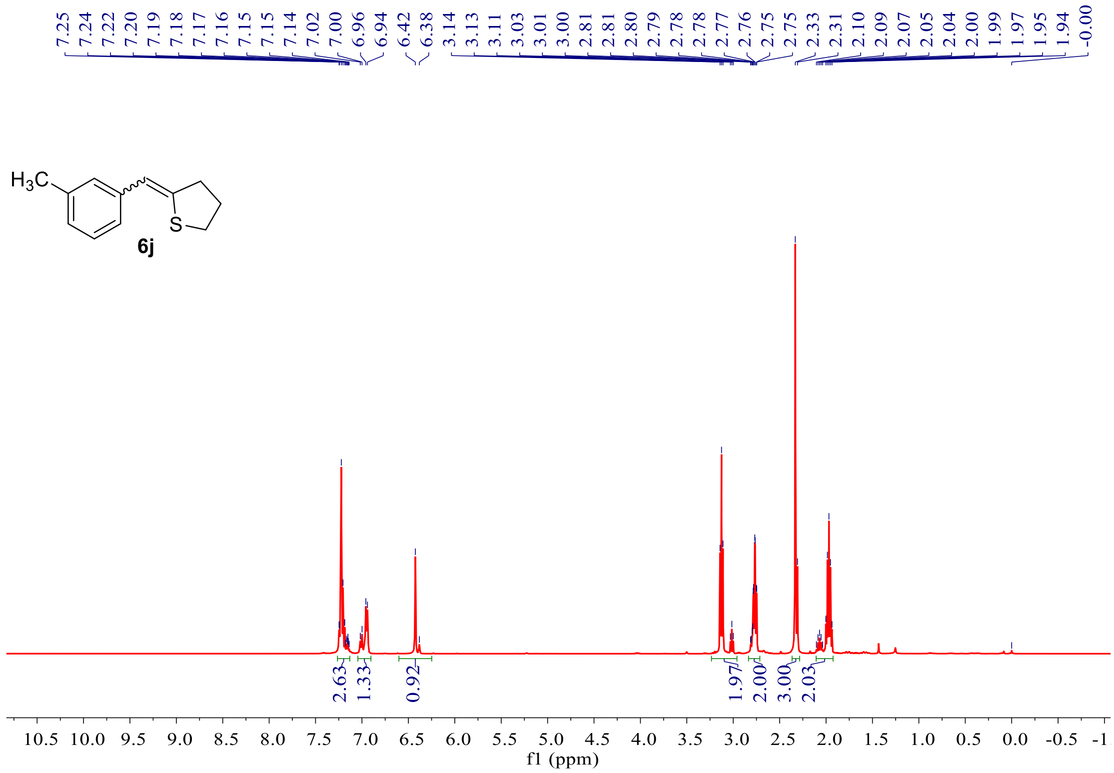
f1 (ppm)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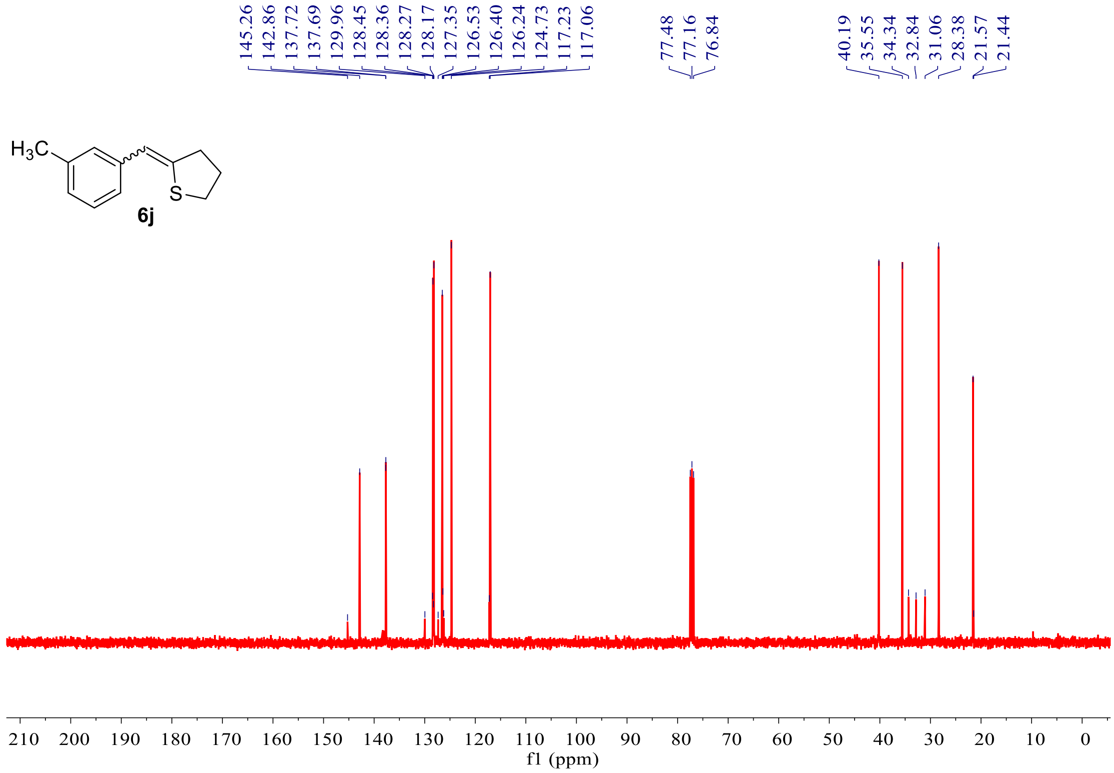
H3C
S
6j
2.63
1.33
0.92
1.97
2.00
3.00
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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77.48 77.16 76.84
40.19 35.55 34.34 32.84 31.06 28.38 21.57 21.44
H3C
S
6j
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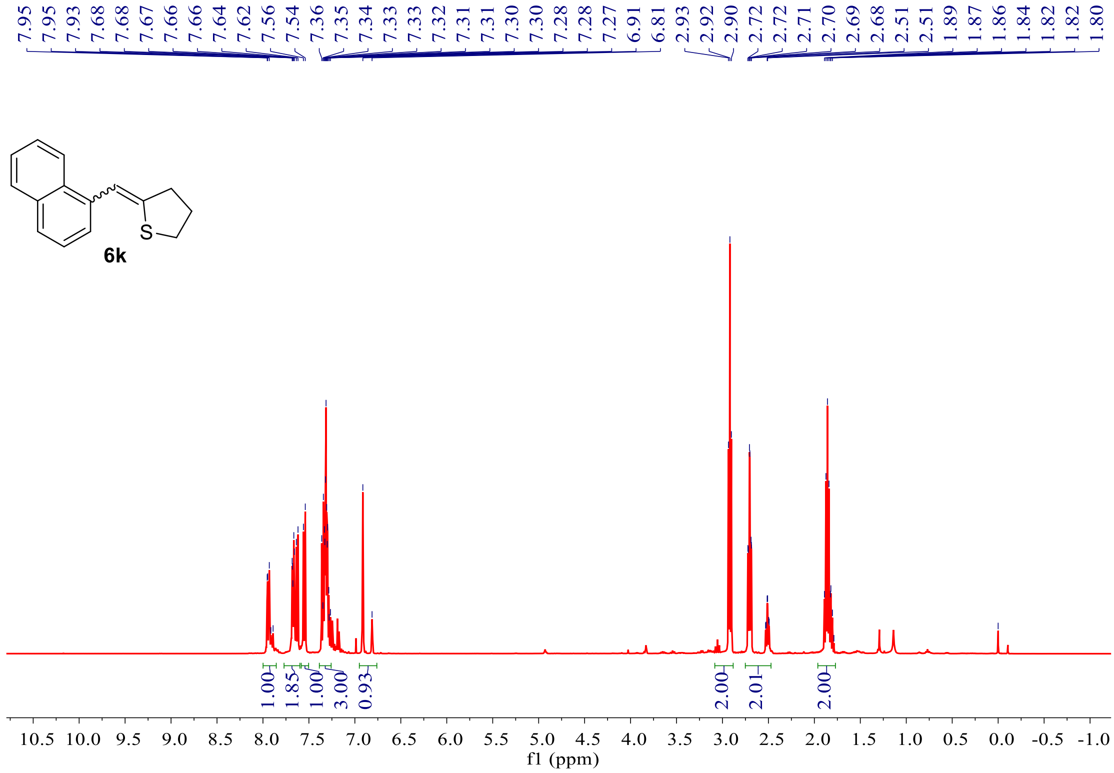
f1 (ppm)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7.56
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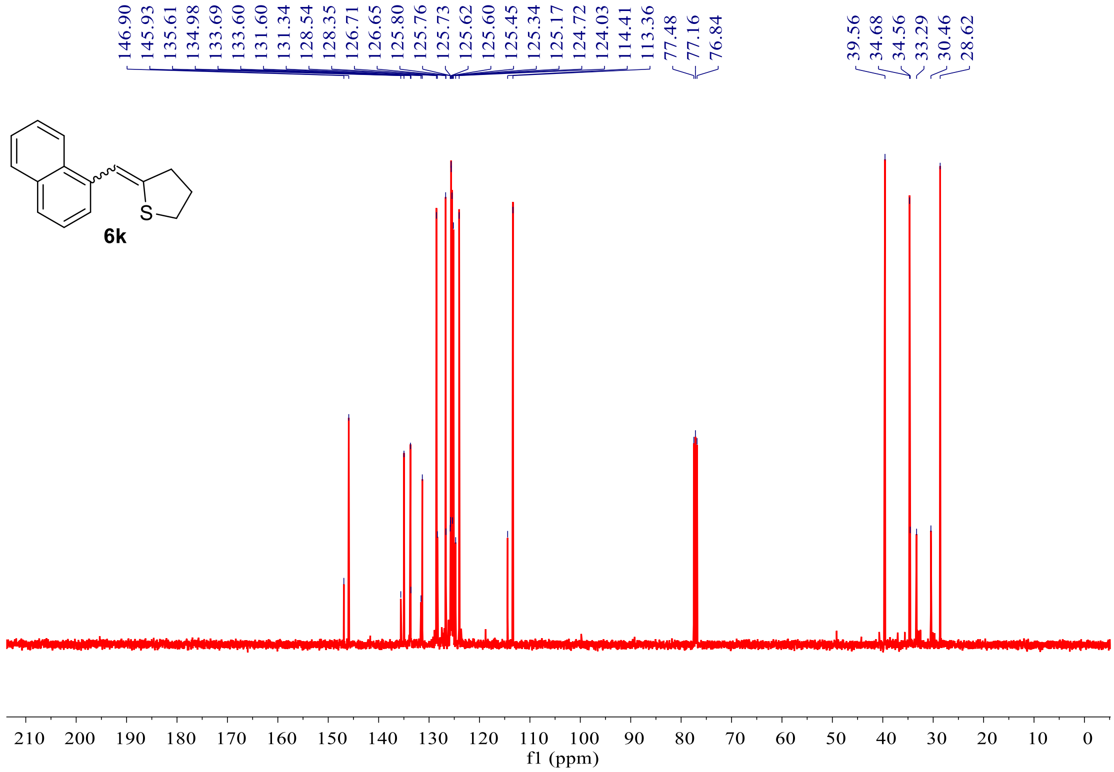
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.28
7.28
7.27
6.91
6.81
2.93
2.92
2.90
2.72
2.72
2.71
2.70
2.69
2.68
2.51
2.51
1.89
1.87
1.86
1.84
1.82
1.82
1.80
S
6k
1.00
1.85
1.00
3.00
0.93
2.00
2.01
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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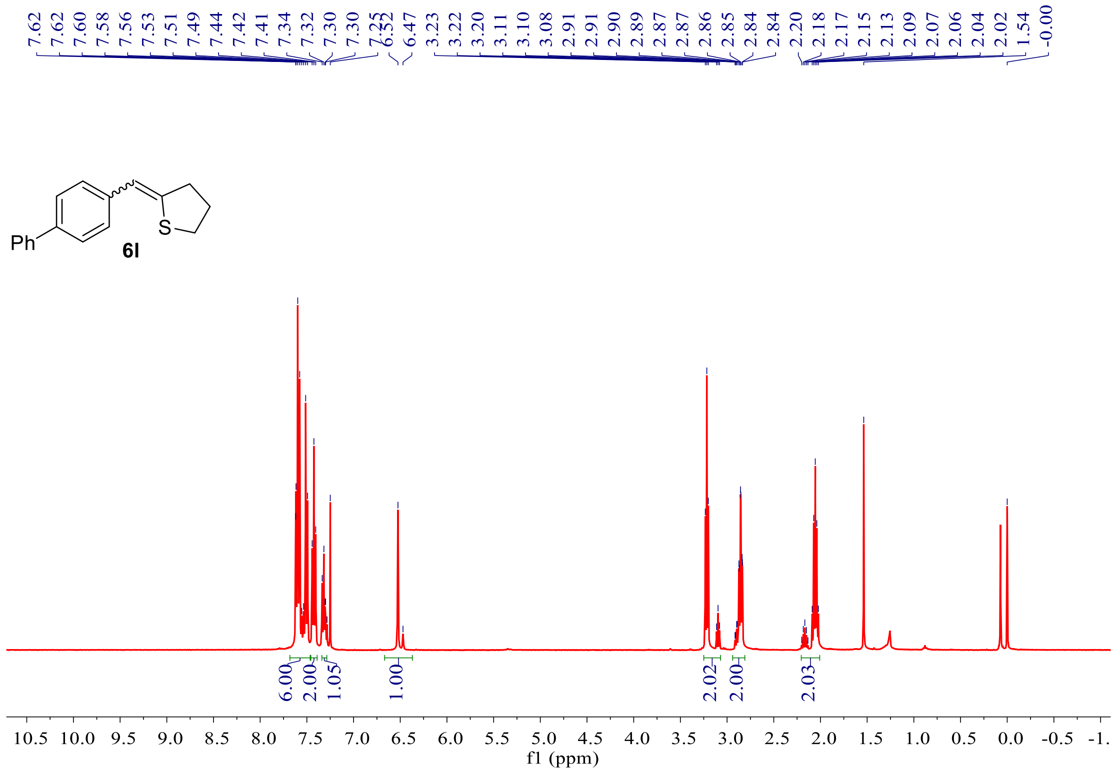
133.60
131.60
131.34
128.54
128.35
126.71
126.65
125.80
125.76
125.73
125.62
125.60
125.45
125.34
125.17
124.72
124.03
114.41
113.36
77.48
77.16
76.84
39.56
34.68
34.56
33.29
30.46
28.62
S
6k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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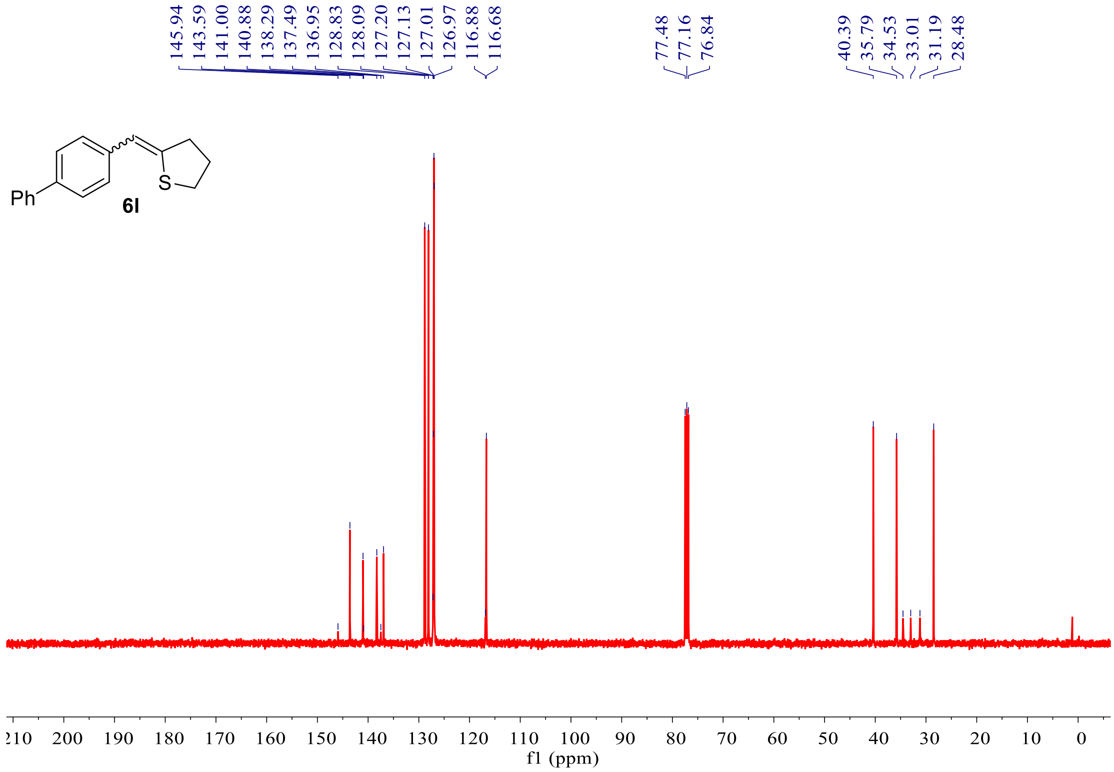
7.41
7.34
7.32
7.30
7.30
7.25
6.52
6.47
3.23
3.22
3.20
3.11
3.10
3.08
2.91
2.91
2.90
2.89
2.87
2.87
2.86
2.85
2.84
2.84
2.20
2.18
2.17
2.15
2.13
2.09
2.07
2.06
2.04
2.02
1.54
-0.00
Ph
S
6l
6.00
2.00
1.05
1.00
2.02
2.00
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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137.49
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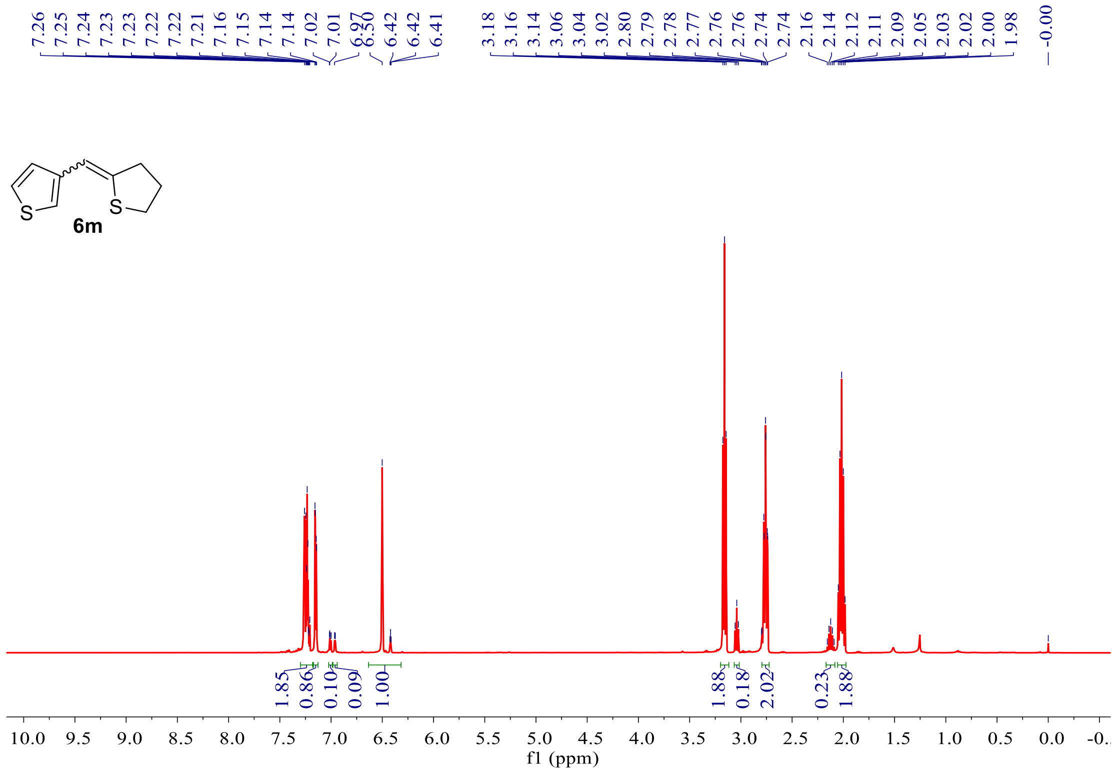
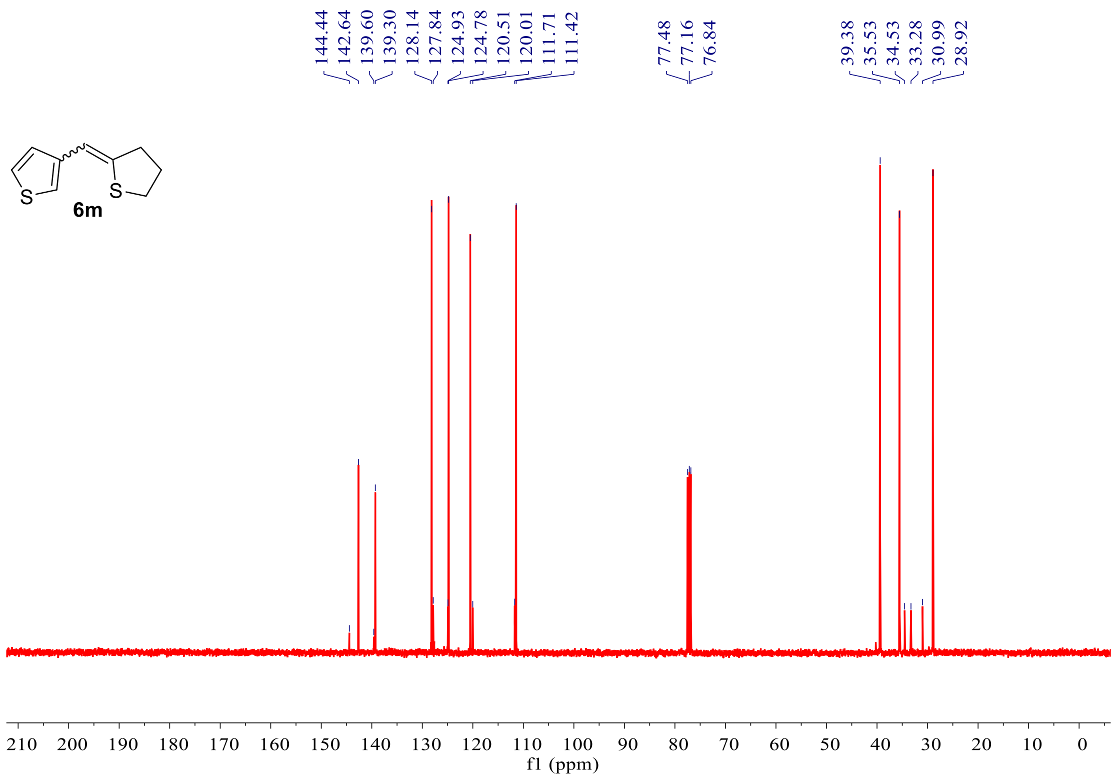
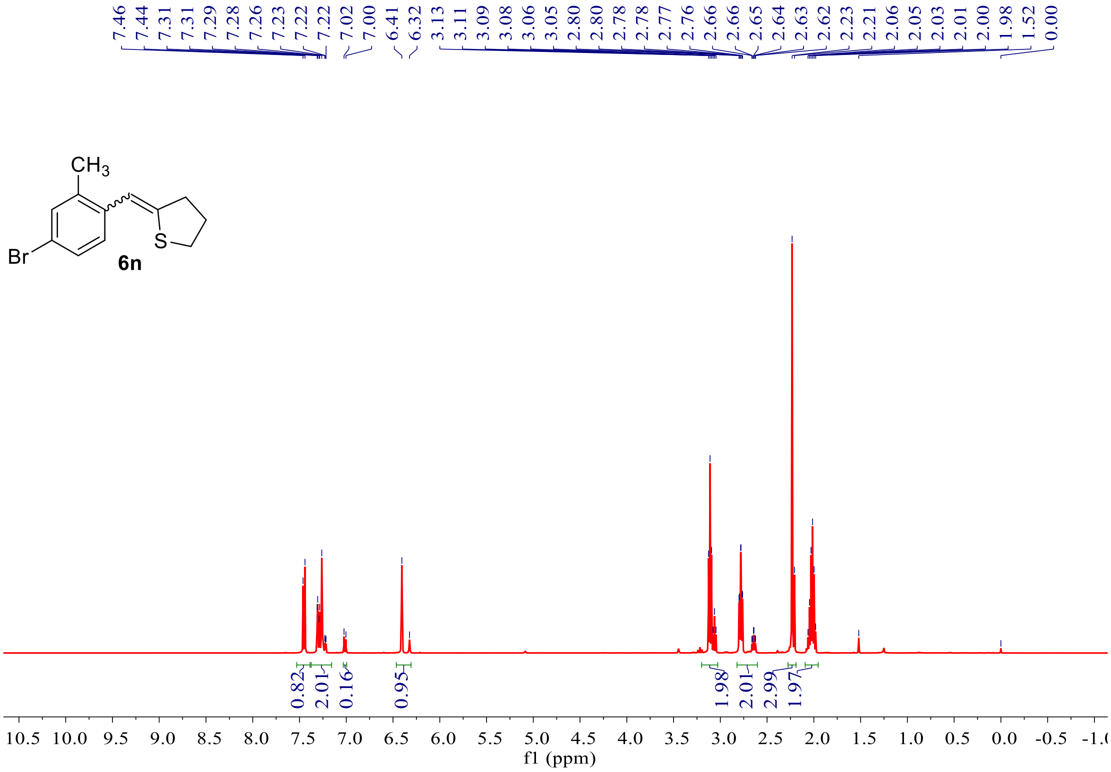
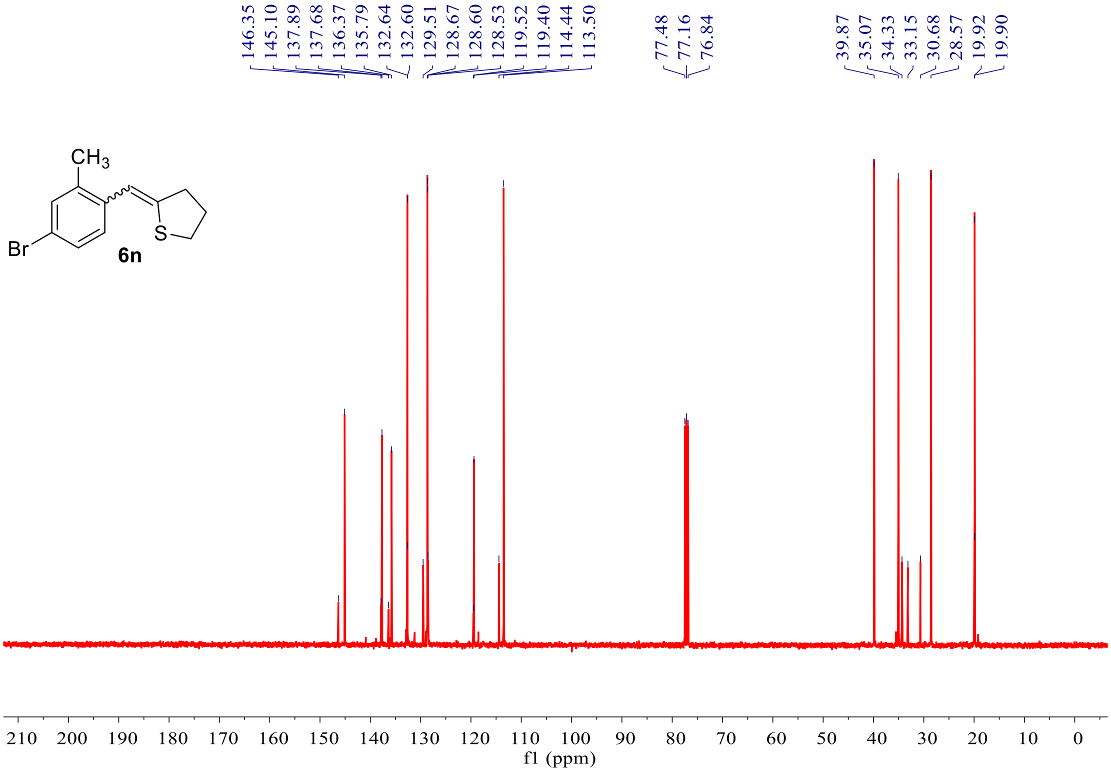
128.83
128.09
127.20
127.13
127.01
126.97
116.88
116.68
77.48
77.16
76.84
40.39
35.79
34.53
33.01
31.19
28.48
Ph
S
6l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)






7.46 7.44 7.31 7.31 7.29 7.28 7.26 7.23 7.22 7.22 7.02 7.00 6.41 6.32 3.13 3.11 3.09 3.08 3.06 3.05 2.80 2.80 2.78 2.78 2.77 2.76 2.66 2.66 2.65 2.64 2.63 2.62 2.23 2.21 2.06 2.05 2.03 2.01 2.00 1.98 1.52 0.00
CH3
Br
S
6n
0.82 2.01 0.16 0.95 1.98 2.01 2.99 1.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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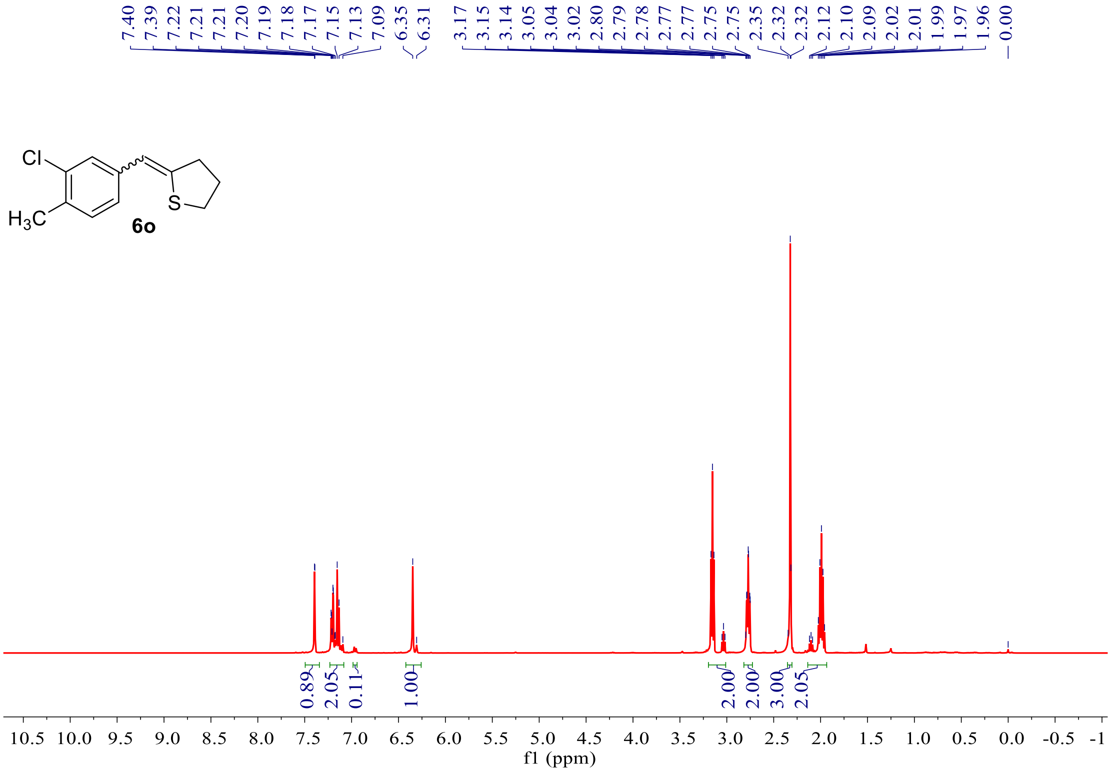
77.48 77.16 76.84
39.87 35.07 34.33 33.15 30.68 28.57 19.92 19.90
CH3
Br
S
6n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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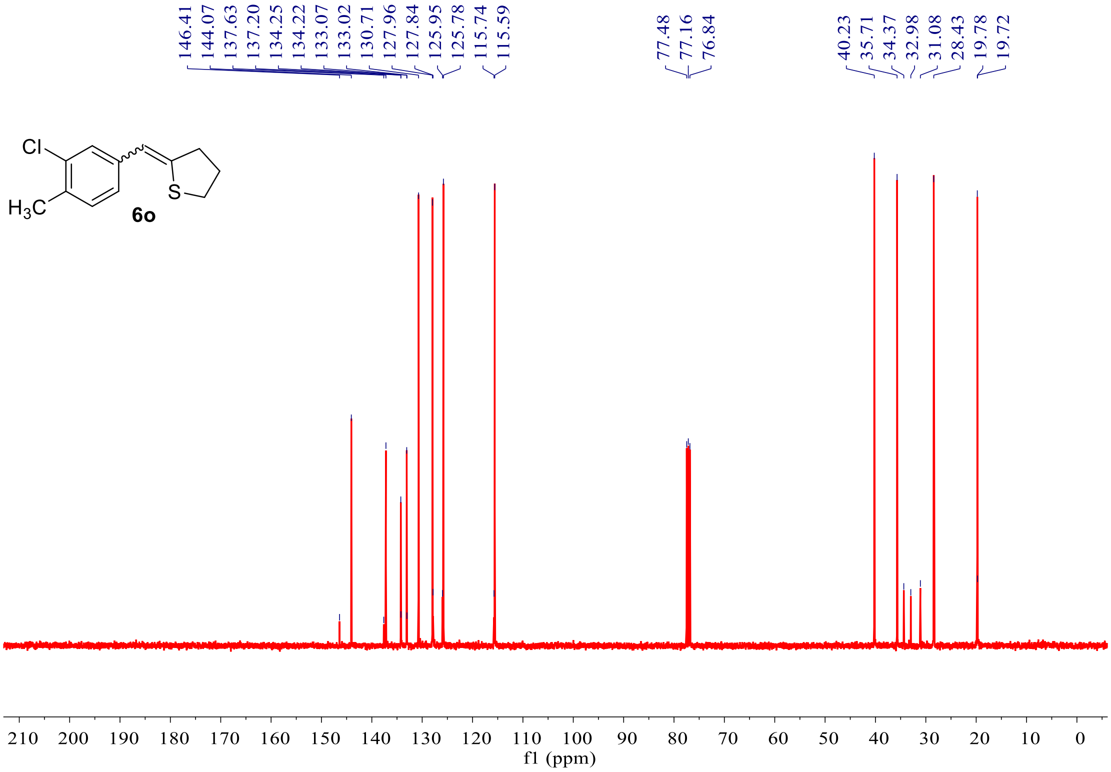
Cl
H3C
S
6o
0.89 2.05 0.11 1.00 2.00 2.00 3.00 2.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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77.48 77.16 76.84
40.23 35.71 34.37 32.98 31.08 28.43 19.78 19.72
Cl
H3C
S
6o
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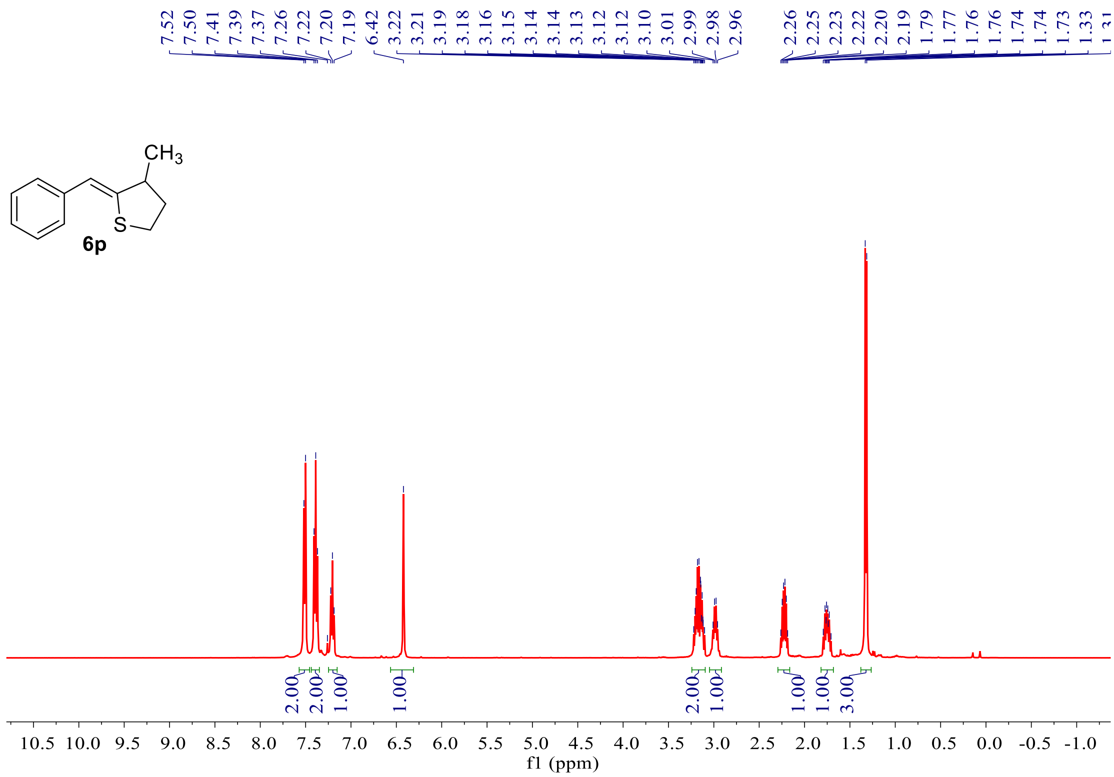
f1 (ppm)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7.20
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6.42
3.22
3.21
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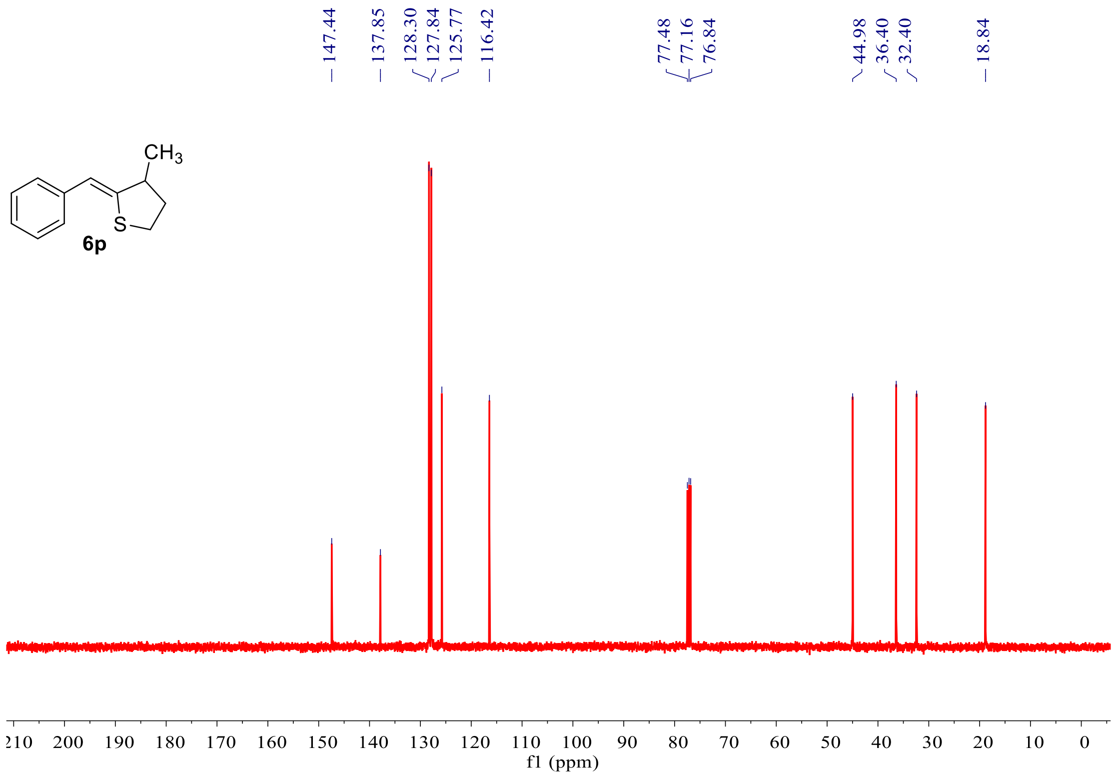
3.13
3.12
3.12
3.10
3.01
2.99
2.98
2.96
2.26
2.25
2.23
2.22
2.20
2.19
1.79
1.77
1.76
1.76
1.74
1.74
1.73
1.33
CH3
S
6p
2.00
2.00
1.00
1.00
2.00
1.00
1.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.16
76.84
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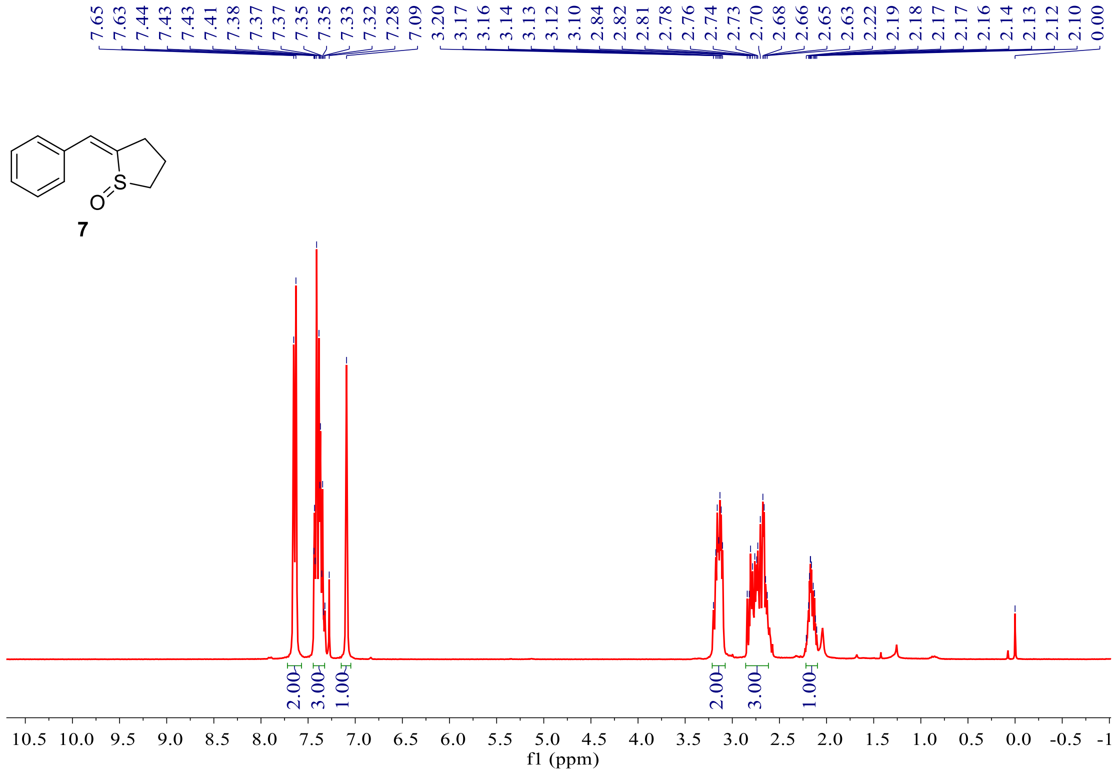
18.84
CH3
S
6p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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7.44
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7.43
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7.37
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7.33
7.32
7.28
7.09
3.20
3.17
3.16
3.14
3.13
3.12
3.10
2.84
2.82
2.81
2.78
2.76
2.74
2.73
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2.65
2.63
2.22
2.19
2.18
2.17
2.17
2.16
2.14
2.13
2.12
2.10
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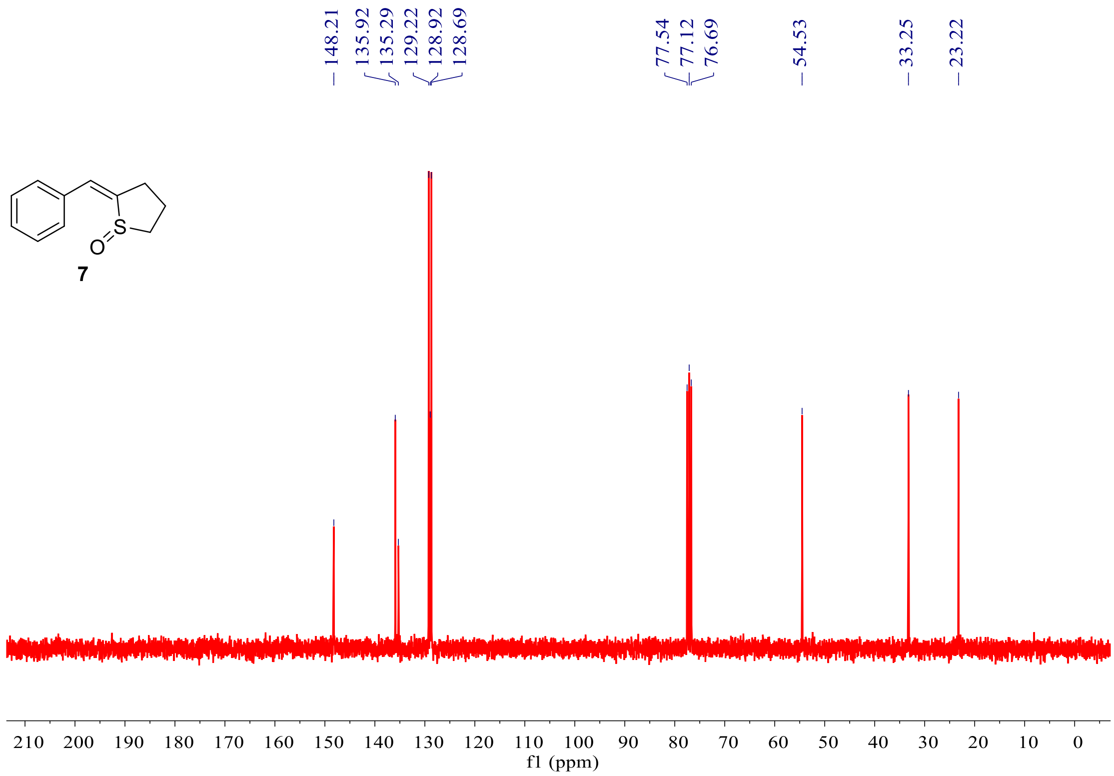
2.00
3.00
1.00
2.00
3.00
1.00
f1 (ppm)



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54.53
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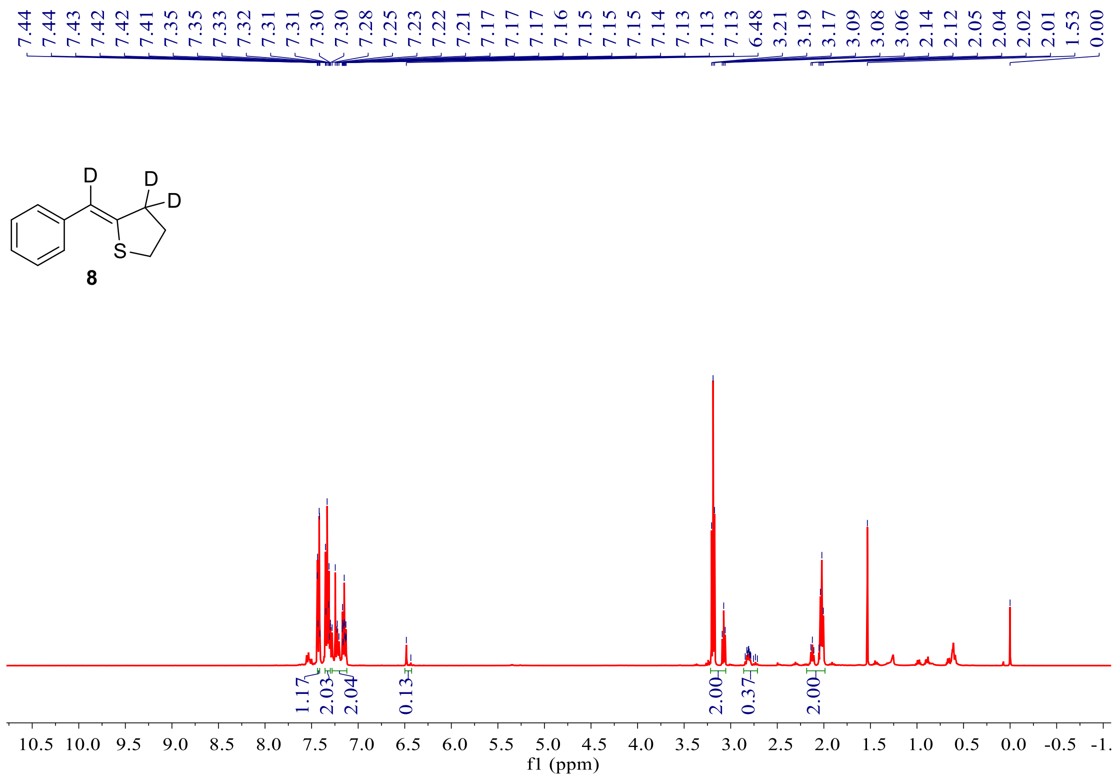
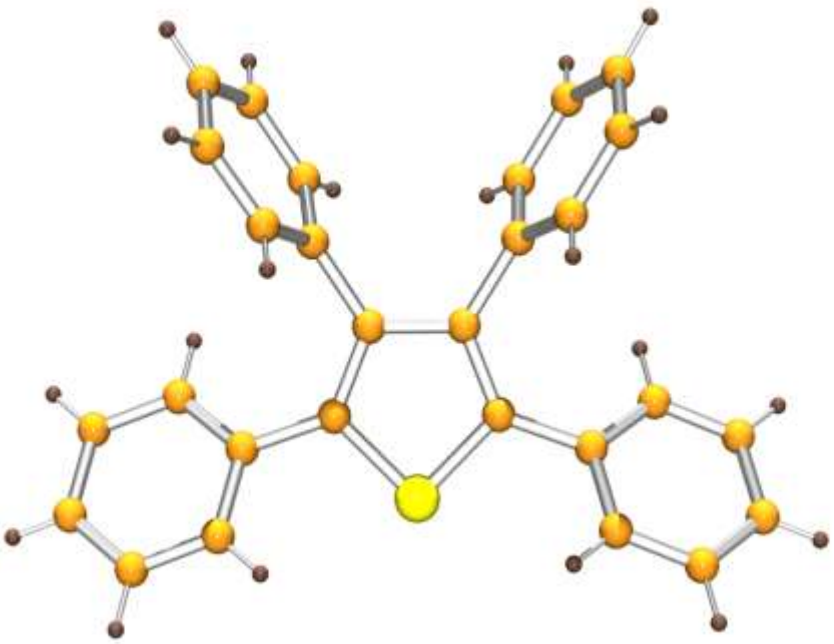
23.22
7
f1 (ppm)



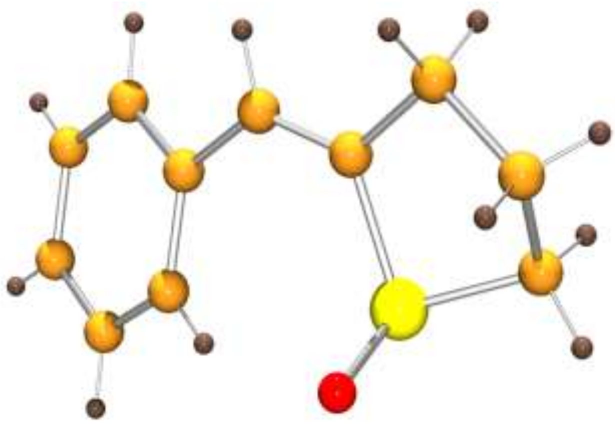
12. X-ray Structure of 3a and 7

12.1. X-ray Structure of 3a



CCDC 1840038 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

12.2. X-ray Structure of 7



CCDC 1840039 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.