Supporting information for

Trisulfur Radical Anion ($S_3^{\bullet-}$) Involved Sulfur Insertion Reaction of 1,3-Enynes: Sulfide Sources Control Chemoselective Synthesis of 2,3,5-trisubstituted Thiophenes and 3-thienyl Disulfides

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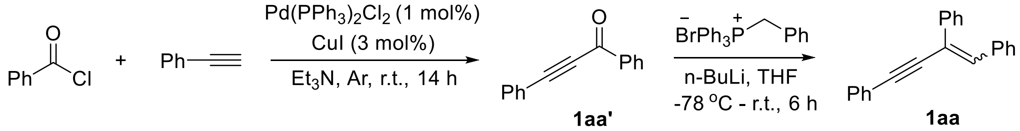
1. General Information

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, 200-300 mesh silica gel was used. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16). 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.

2. Synthesis of But-1-en-3-yne-1,2,4-triyltribenzene 1aa

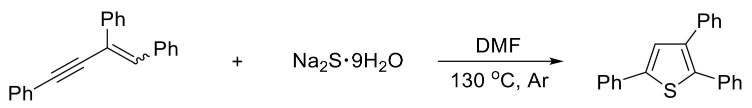


1aa' **1aa**

To a 50 mL Schlenk tube was added CuI (0.0286 g, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (0.0351 g, 0.05 mmol), and Et_3N (10 mL) under an Ar atmosphere. Then, ethynylbenzene (0.5107 g, 5.0 mmol, 1.0 equiv) was added. Benzoyl chloride (0.9137 g, 6.5 mmol, 1.3 equiv) was added dropwise to the reaction mixture. After stirred at r.t. for 14 hours, the mixture was quenched with H_2O (10 mL). The aqueous layer was extracted with AcOEt. The combined organic layer was washed with brine, and dried over Na_2SO_4, then, filtered. After concentration under vacuum, the crude mixture was subjected to silica gel column chromatography (hexane/AcOEt = 20:1) to obtain 1,3-diphenylprop-2-yn-1-one **1aa'**(4.25 mmol, 85%) as yellow 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 Benzyltriphenylphosphonium bromide (2.2533 g, 5.2 mmol, 1.3 equiv) and dry THF (10 mL). After cooling to –78 ℃, n-BuLi (2.5 M, 1.92 mL, 4.8 mmol, 1.2 equiv) was added dropwise to the reaction mixture at –78 ℃. The mixture was stirred at r.t. for 1 h. Then, a solution of 1,3-diphenylprop-2-yn-1-one **1aa'** (0.8250 g, 4.0 mmol, 1.0 equiv) in dry THF (5 mL) was added. And the mixture was further stirred at r.t. for 5 h. The reaction was quenched by adding saturated NH_4Cl 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 (hexane/AcOEt = 100:1) to afford But-1-en-3-yne-1,2,4-triyltribenzene **1aa** (3.2 mmol, 80%) as a light yellow solid.

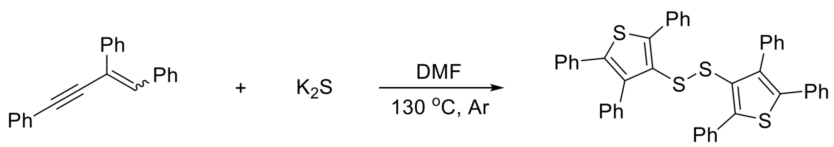
3. Synthesis of 2,3,5-triphenylthiophene 3aa



1aa 2b 3aa

A mixture of But-1-en-3-yne-1,2,4-triyltribenzene **1aa** (0.3 mmol) and $Na_2S\cdot 9H_2O$ **2b** (1.2 mmol) in 2.0 mL DMF was stirred under an Ar atmosphere at 130 ℃ for 7 h. After completion of the reaction, as indicated by TLC, water (15 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 **3aa** in 87% yield. All remaining 2,3,5-trisubstituted thiophenes (except **3ag**) were prepared using a procedure similar to that used to synthesize **3aa**. The **3ag** was purified by flash column chromatography (hexane/EtOAc = 4:1).

4. Synthesis of 1,2-bis(2,4,5-triphenylthiophen-3-yl)disulfane 4aa

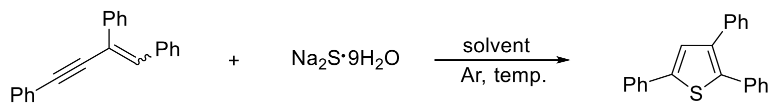


1aa 2a 4aa

A mixture of But-1-en-3-yne-1,2,4-triyltribenzene **1aa** (0.5 mmol) and K_2S **2a** (2.0 mmol) in 2.0 mL DMF was stirred under an Ar atmosphere at 130 ℃ for 5 h. After completion of the reaction, as indicated by TLC, water (15 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 hexane/EtOAc (100:1) on silica gel to afford **4aa** in 73% yield. All remaining 3-thienyl disulfides (except **4ag**) were prepared using a procedure similar to that used to synthesize **4aa**. The **4ag** was purified by flash column chromatography (hexane/EtOAc = 3:1).

5. Screenings of two Reactions' Conditions

Table 1. Optimization for the Formation of 3aa



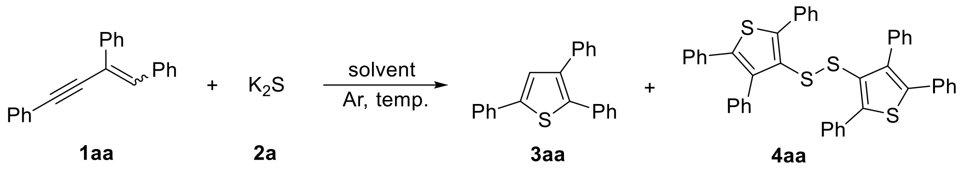
1aa 2b 3aa

Entry	Slovent (2.0 mL)	Tempurature (ºC)	Time (h)	Yield[b] (%) 3aa
1	DMF	130	8	87
2[c]	DMF	130	8	70
3	DMSO	130	8	54
4	DMA	130	8	78
5	DMF	60	8	0

6	DMF	110	8	80
7	DMF	140	8	85
8	DMF	130	5	73
9	**DMF**	**130**	**7**	**87**

[a]Reaction Conditions: **1aa** (0.3 mmol), **2b** (1.2 mmol), slovent (2.0 mL), under Ar. [b]Isolated yield. [c]Without Ar protecting.

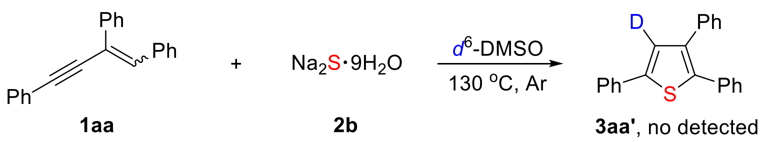
Table 2. Optimization for the Formation of 4aa

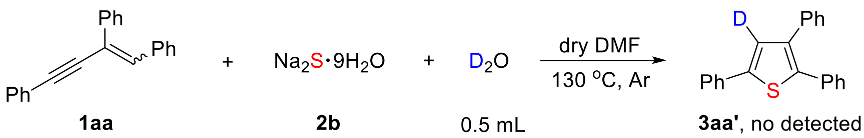


Entry	Slovent (2.0 mL)	Tempurature (°C)	Time (h)	Yield[b] (%) 3aa	4aa
1	DMF	130	8	24	73
2[c]	DMF	130	8	messy	56
3	DMSO	130	8	36	53
4	DMA	130	8	57	42
5	DMF	60	8	15	13
6	DMF	110	8	28	59
7	DMF	140	8	24	70
8	DMF	130	6	24	72
9	**DMF**	**130**	**5**	**24**	**73**

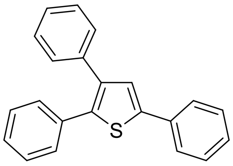
[a]Reaction conditions: **1aa** (0.3 mmol), **2a** (1.2 mmol), slovent (2.0 mL), under Ar. [b]Isolated yield. [c]Without Ar protecting.

6. Deuterated Experiment





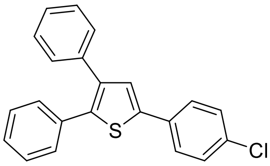
7. Spectroscopic Data of Compounds



3aa

2,3,5-triphenylthiophene (3aa)

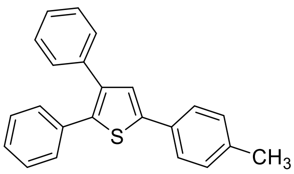
Yield = 87% (81.5 mg). White solid. Mp: 135.2-136.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.44 – 7.23 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.7, 139.1, 138.1, 136.7, 134.3, 134.2, 129.3, 129.2, 129.1, 128.6, 128.5, 127.8, 127.6, 127.2, 126.6, 125.7. **IR (ATR)**: ν = 1597, 1484, 1071, 846, 756, 695, 464 cm^{-1}; **HRMS** (EI): calcd. for $C_{22}H_{16}S$ $[M+H]^+$: 313.1051, found: 313.1044.



3ab

5-(4-chlorophenyl)-2,3-diphenylthiophene (3ab)

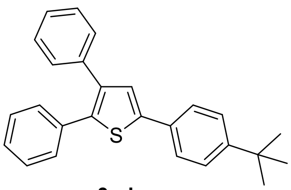
Yield = 73% (76.0 mg). White solid. Mp: 161.4-162.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.33 – 7.17 (m, 13H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.2, 139.2, 138.4, 136.5, 134.1, 133.4, 132.6, 129.2, 129.2, 129.1, 128.6, 128.5, 127.7, 127.2, 126.9, 126.8. **IR (ATR)**: ν = 2357, 1443, 1090, 1013, 828, 759, 695, 499 cm^{-1}; **HRMS** (EI): calcd. for $C_{22}H_{15}ClS$ $[M+H]^+$: 347.0661, found: 347.0670.



3ac

2,3-diphenyl-5-(p-tolyl)thiophene (3ac)

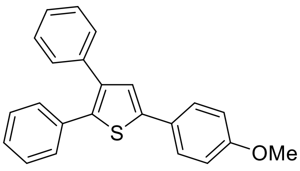
Yield = 74% (72.5 mg). White solid. **Mp**: 109.3-110.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.42 – 7.10 (m, 13H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.9, 139.0, 137.6, 137.5, 136.8, 134.4, 131.4, 129.7, 129.2, 129.2, 128.6, 128.5, 127.5, 127.1, 126.1, 125.6, 21.3. **IR (ATR)**: ν = 1597, 1487, 1069, 809, 757, 691, 481 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{16}S$ $[M+H]^+$: 327.1207, found: 327.1202.



3ad

5-(4-(tert-butyl)phenyl)-2,3-diphenylthiophene (3ad)

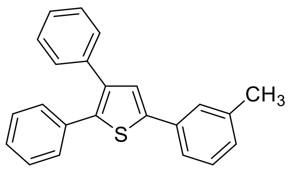
Yield = 72% (79.6 mg). Light yellow solid. Mp: 100.5-101.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.44 – 7.39 (m, 2H), 7.37 – 7.22 (m, 11H), 1.36 – 1.32 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 142.8, 139.0, 137.6, 136.8, 134.5, 131.5, 129.3, 129.2, 128.6, 128.5, 127.5, 127.1, 126.3, 126.0, 125.5, 34.8, 31.4. **IR (ATR)**: ν = 2949, 1490, 823, 755, 695, 532, 507 cm^{-1}; **HRMS** (EI): calcd. for $C_{26}H_{24}S$ $[M+H]^+$: 369.1677, found: 369.1674.



3ae

5-(4-methoxyphenyl)-2,3-diphenylthiophene (3ae)

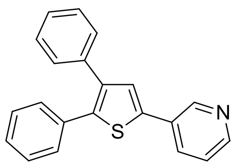
Yield = 81% (83.2 mg). White solid. Mp: 116.7-117.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.20 (m, 11H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 142.7, 139.0, 137.1, 136.8, 134.4, 129.2(3), 129.1(9), 128.6, 128.5, 127.4, 127.0(7), 127.0(6), 127.0(1), 125.7, 114.5, 55.5. **IR (ATR)**: ν = 1599, 1488, 1251, 1029, 827, 693, 499 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}OS$ $[M+H]^+$: 343.1157, found: 343.1151.



3af

2,3-diphenyl-5-(m-tolyl)thiophene (3af)

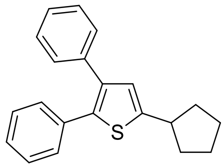
Yield = 78% (76.4 mg). Light yellow solid. Mp: 64.9-66.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.27 (m, 5H), 7.27 – 7.16 (m, 7H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 139.0, 138.6, 137.9, 136.7, 134.4, 134.1, 129.2, 129.2, 128.9, 128.5(4), 128.4(8), 127.5, 127.1, 126.5, 126.4, 122.8, 21.6. **IR (ATR)**: ν = 1599, 1481, 1442, 1068, 781, 692, 500, 438 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}S$ $[M+H]^+$: 327.1207, found: 327.1205.



3ag

3-(4,5-diphenylthiophen-2-yl)pyridine (3ag)

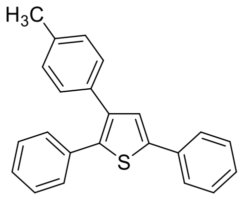
Yield = 83% (78.0 mg). White solid. Mp: 97.9-98.6 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.54 (s, 1H), 7.93 – 7.88 (m, 1H), 7.41 (s, 1H), 7.38 – 7.26 (m, 11H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 146.6, 139.3(1), 139.2(8), 138.5, 136.2, 133.8, 132.6, 130.2, 129.2, 129.1, 128.6, 128.5, 127.8, 127.6, 127.3, 123.7. **IR (ATR)**: ν = 1474, 1416, 1021, 812, 767, 700, 613, 496 cm^{-1}; **HRMS** (EI): calcd. for $C_{21}H_{15}NS$ $[M+H]^+$: 314.1003, found: 314.1002.



3ah

5-cyclopentyl-2,3-diphenylthiophene (3ah)

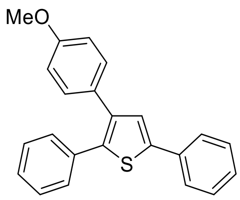
Yield = 82% (74.9 mg). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 10H), 6.87 (d, *J* = 1.0 Hz, 1H), 3.25 (d, *J* = 8.3 Hz, 1H), 2.15 (td, *J* = 6.7, 6.0, 4.0 Hz, 1H), 1.90 – 1.63 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 137.6, 137.1, 135.6, 134.9, 129.3, 129.2, 128.5, 128.4, 127.1, 126.8, 126.4, 41.4, 35.5, 25.3. **IR (ATR)**: ν =2950, 1599, 1496, 1068, 837, 755, 693, 548 cm^{-1}; **HRMS** (EI): calcd. for $C_{21}H_{20}S$ $[M+H]^+$: 305.1364, found: 305.1369.



3ba

2,5-diphenyl-3-(p-tolyl)thiophene (3ba)

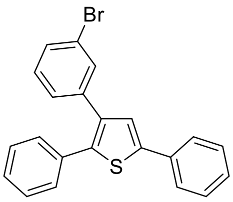
Yield = 87% (85.2 mg). White solid. Mp: 90.1-91.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H), 7.42 – 7.31 (m, 5H), 7.30 – 7.17 (m, 6H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.5, 139.1, 137.7, 136.8, 134.5, 134.3, 133.8, 129.2(6), 129.2(5), 129.1, 129.0, 128.6, 127.7, 127.5, 126.7, 125.7, 21.3. **IR (ATR)**: ν = 1593, 1485, 1025, 813, 760, 684, 548, 463 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}S$ $[M+H]^+$: 327.1207, found: 327.1201.



3bb

3-(4-methoxyphenyl)-2,5-diphenylthiophene (3bb)

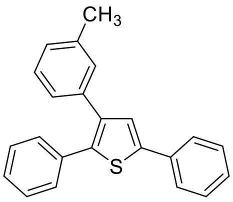
Yield = 74% (76.0 mg). White solid. Mp: 80.6-81.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.52 (m, 2H), 7.44 – 7.30 (m, 5H), 7.30 – 7.20 (m, 6H), 6.86 – 6.76 (m, 2H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 142.5, 138.7, 137.3, 134.5, 134.3, 130.3, 129.2, 129.1, 129.0, 128.6, 127.7, 127.4, 126.6, 125.7, 114.0, 55.31. **IR (ATR)**: ν = 1595, 1486, 1286, 1173, 1031, 818, 692, 462 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}OS$ $[M+H]^+$: 343.1157, found: 343.1161.



3bc

3-(3-bromophenyl)-2,5-diphenylthiophene (3bc)

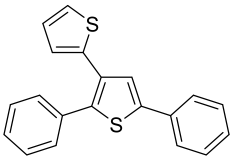
Yield = 67% (78.7 mg). White solid. Mp: 91.2-92.4 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.51 (t, *J* = 1.8 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.33 – 7.23 (m, 7H), 7.18 – 7.14 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.0, 138.9, 138.6, 137.3, 134.0, 133.8, 131.9, 130.1, 130.0, 129.2, 129.1, 128.7, 127.9(3), 127.8(9), 127.8(6), 126.1, 125.7, 122.6. **IR (ATR)**: ν = 1590, 1476, 1069, 788, 689, 615, 486, 438 cm^{-1}; **HRMS** (EI): calcd. for $C_{22}H_{15}BrS$ $[M+H]^+$: 391.0156, found: 391.0145.



3bd

2,5-diphenyl-3-(m-tolyl)thiophene (3bd)

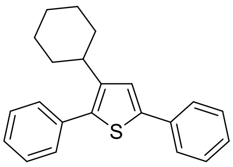
Yield = 77% (75.4 mg). White solid. Mp: 75.9-76.8 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.41 – 7.30 (m, 5H), 7.27 – 7.02 (m, 8H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.5, 139.2, 138.1, 138.0, 136.6, 134.4, 134.2, 129.8, 129.2, 129.1, 128.5, 128.4, 127.9, 127.7, 127.5, 126.7, 126.4, 125.7, 21.56. **IR (ATR)**: ν = 1597, 1481, 1031, 789, 755, 689, 463,440 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}S$ $[M+H]^+$: 327.1207, found: 327.1213.



3be

2',5'-diphenyl-2,3'-bithiophene (3be)

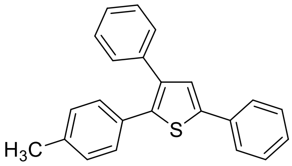
Yield = 89% (85.0 mg). White solid. Mp: 91.4-92.5 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 2H), 7.47 – 7.21 (m, 9H), 7.15 – 7.10 (m, 1H), 6.95 – 6.84 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 138.3, 138.1, 134.0, 133.9, 131.7, 129.8, 129.1, 128.6, 128.1, 127.9, 127.3, 125.9, 125.8, 125.7, 124.9. **IR (ATR)**: ν = 1485, 1216, 827, 762, 694, 486 cm^{-1}; **HRMS** (EI): calcd. for $C_{20}H_{14}S_2$ $[M+H]^+$: 319.0615, found: 319.0613.



3bf

3-cyclohexyl-2,5-diphenylthiophene (3bf)

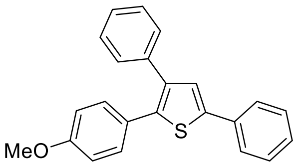
Yield = 76% (72.6 mg). White solid. Mp: 82.6-84.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 2H), 7.47 – 7.24 (m, 9H), 2.84 – 2.69 (m, 1H), 1.94 – 1.60 (m, 6H), 1.58 – 1.30 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 142.6, 136.8, 134.7, 131.7, 129.6, 129.0, 128.7, 127.5, 127.4, 125.7, 123.5, 38.1, 34.8, 26.8, 26.3. **IR (ATR)**: ν =2921, 1594, 1486, 1442, 838, 755, 495 cm^{-1}; **HRMS** (EI): calcd. for $C_{22}H_{22}S$ $[M+H]^+$: 319.1520, found: 319.1529.



3ca

3,5-diphenyl-2-(p-tolyl)thiophene (3ca)

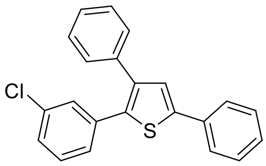
Yield = 74% (72.5 mg). White solid. **Mp**: 99.9-101.0 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.6 Hz, 2H), 7.49 – 7.27 (m, 11H), 7.16 – 7.10 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 138.7, 137.4, 136.9, 134.3, 131.4, 129.3, 129.2, 129.1, 129.0, 128.5, 127.6, 127.0, 126.6, 125.7, 21.34. **IR (ATR)**: ν = 1485, 1028, 816, 755, 695, 517, 475 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}S$ $[M+H]^+$: 327.1207, found: 327.1214.



3cb

2-(4-methoxyphenyl)-3,5-diphenylthiophene (3cb)

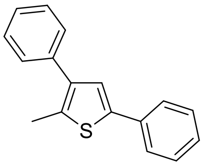
Yield = 71% (72.9 mg). White solid. Mp: 78.3-79.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.55 (m, 2H), 7.42 – 7.21 (m, 11H), 6.87 – 6.70 (m, 2H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 141.9, 138.4, 138.1, 136.8, 134.3, 130.5, 129.2, 129.0, 128.5, 127.6, 127.0, 126.8, 126.5, 125.6, 114.1, 55.34. **IR (ATR)**: ν = 1599, 1501, 1179, 1029, 825, 754, 528, 477 cm^{-1}; **HRMS** (EI): calcd. for $C_{23}H_{18}OS$ $[M+H]^+$: 343.1157, found: 343.1159.



3cc

2-(3-chlorophenyl)-3,5-diphenylthiophene (3cc)

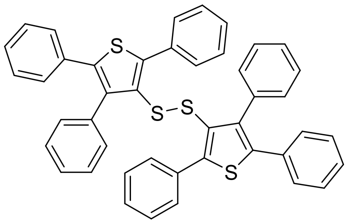
Yield = 66% (68.7 mg). White solid. **Mp**: 74.5-76.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.40 – 7.23 (m, 10H), 7.20 – 7.09 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 139.9, 136.2, 136.1(1), 136.1(0), 134.4, 133.9, 129.7, 129.1, 129.0, 128.6, 127.9, 127.5, 127.4(1), 127.3(8), 126.6, 125.7. **IR (ATR)**: ν = 1588, 1478, 1095, 788, 752, 693, 542, 440 cm^{-1}; **HRMS** (EI): calcd. for $C_{22}H_{15}ClS$ $[M+H]^+$: 347.0661, found: 347.0655.



3cd

2-methyl-3,5-diphenylthiophene (3cd)

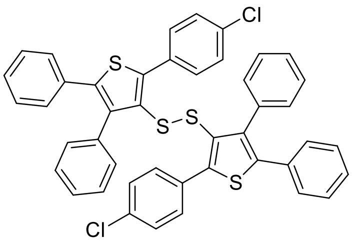
Yield = 31% (23.3 mg). Light yellow solid. **Mp**: 56.7-57.4 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.45 – 7.29 (m, 7H), 7.28 – 7.19 (m, 2H), 2.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.1, 139.8, 136.8, 134.5, 134.0, 129.0, 128.7, 128.6, 127.3, 127.0, 125.6, 125.2, 14.46. **IR (ATR)**: ν = 2921, 1598, 1445, 1073, 844, 755, 590, 468 cm^{-1}; **HRMS** (EI): calcd. for $C_{17}H_{14}S$ $[M+H]^+$: 251.0894, found: 251.0891.



4aa

1,2-bis(2,4,5-triphenylthiophen-3-yl)disulfane (4aa)

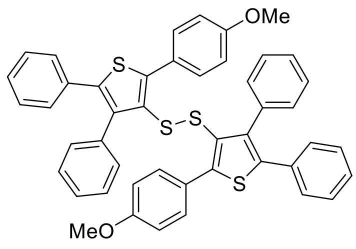
Yield = 73% (75.2 mg). White solid. **Mp**: 119.8-120.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 10H), 7.20 (m, 12H), 7.14 – 7.09 (m, 4H), 7.01 – 6.88 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 142.3, 138.9, 136.0, 133.9, 133.4, 131.2, 129.9, 129.0, 128.4, 128.3, 128.2, 127.9, 127.5, 127.2. **IR (ATR)**: ν = 1444, 1029, 748, 692, 521, 409 cm^{-1}.



4ab

1,2-bis(2-(4-chlorophenyl)-4,5-diphenylthiophen-3-yl)disulfane (4ab)

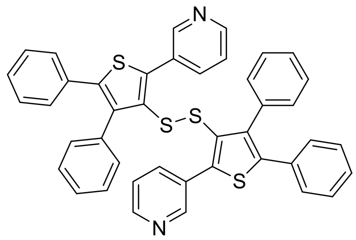
Yield = 35% (39.7 mg). Pale yellow solid. **Mp**: 140.9-141.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 8H), 7.24 – 7.18 (m, 12H), 7.12 – 7.07 (m, 4H), 6.93 (d, *J* = 4.8 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 142.4, 139.3, 135.8, 134.3, 133.5, 131.8, 131.1, 130.9, 129.0, 128.6, 128.0, 127.8, 127.3. **IR (ATR)**: ν = 1497, 1090, 1013, 829, 696, 498, 416 cm^{-1}.



4ad

1,2-bis(2-(4-methoxyphenyl)-4,5-diphenylthiophen-3-yl)disulfane (4ad)

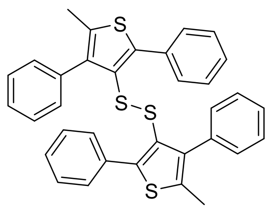
Yield = 62% (69.5 mg). Pale yellow solid. **Mp**: 180.3-181.2 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 4H), 7.23 – 7.16 (m, 12H), 7.14 – 7.09 (m, 4H), 7.02 – 6.94 (m, 4H), 6.88 – 6.84 (m, 4H), 3.72 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 147.9, 142.3, 138.1, 136.2, 133.9, 131.2, 131.0, 128.9, 128.4, 128.0, 127.8, 127.4, 127.1, 126.0, 113.8, 55.4. **IR (ATR)**: ν = 1515, 1249, 1031, 830, 692, 510 cm^{-1}.



4ag

1,2-bis(4,5-diphenyl-2-(pyridin-3-yl)thiophen-3-yl)disulfane (4ag)

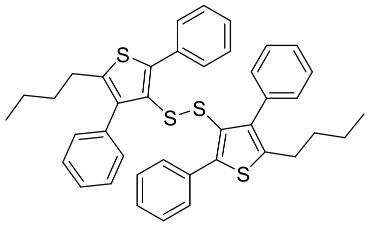
Yield = 43% (44.4 mg). Pale yellow solid. **Mp**: 173.4-174.1 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.4 Hz, 2H), 8.58 – 8.52 (m, 2H), 7.67 – 7.62 (m, 2H), 7.31 – 7.19 (m, 14H), 7.14 – 7.08 (m, 4H), 7.00 – 6.85 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 149.0, 143.6, 142.3, 140.1, 136.8, 135.5, 133.3, 131.0, 129.5, 129.0, 128.5, 128.0, 127.9, 127.4, 123.0. **IR (ATR)**: ν = 1443, 1025, 760, 695, 628, 403 cm^{-1}.



4cd

1,2-bis(5-methyl-2,4-diphenylthiophen-3-yl)disulfane (4cd)

Yield = 38% (32.1 mg). yellow solid. **Mp**: 116.5-117.3 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 12H), 7.24 – 7.18 (m, 4H), 6.95 – 6.87 (m, 4H), 2.18 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.5, 142.9, 135.9, 134.4, 133.7, 130.7, 129.9, 128.1, 127.7, 127.6, 127.0, 14.18. **IR (ATR)**: ν = 1482, 1072, 750, 691, 504 cm^{-1}.

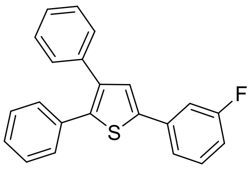


4ce

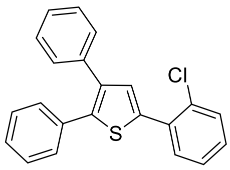
1,2-bis(5-butyl-2,4-diphenylthiophen-3-yl)disulfane (4ce)

Yield = 61% (59.6 mg). pale brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 16H), 7.06 – 6.73 (m, 4H), 2.53 (t, J = 7.8 Hz, 4H), 1.54 – 1.46 (m, 4H), 1.26 (q, J = 7.7 Hz, 4H), 0.82 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 142.7, 140.9, 136.2, 133.9, 130.8, 129.9, 128.2, 127.8, 127.7, 127.1, 127.0, 33.84, 28.49, 22.40, 13.89. **IR (ATR)**: ν = 1600, 1442, 1071, 750, 692, 503 cm^{-1}.

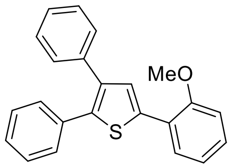
8. Unsuccessful examples



3ai



3aj



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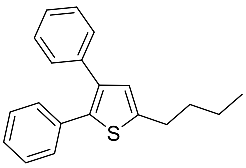
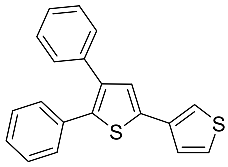
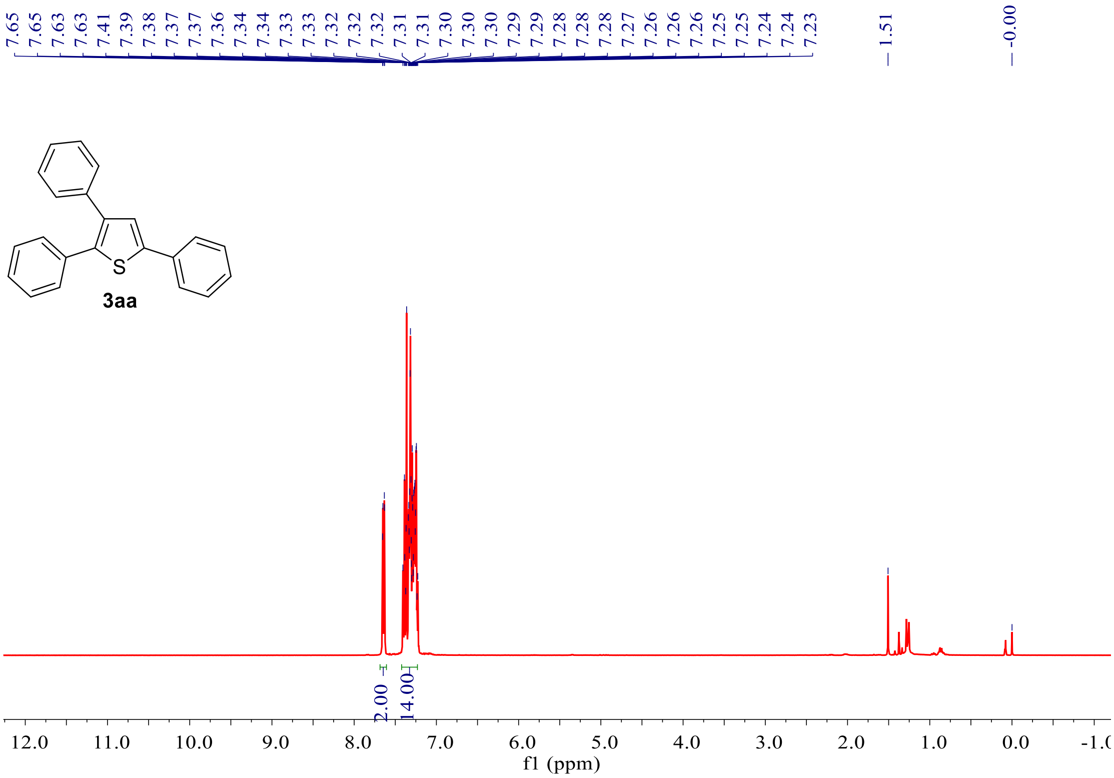


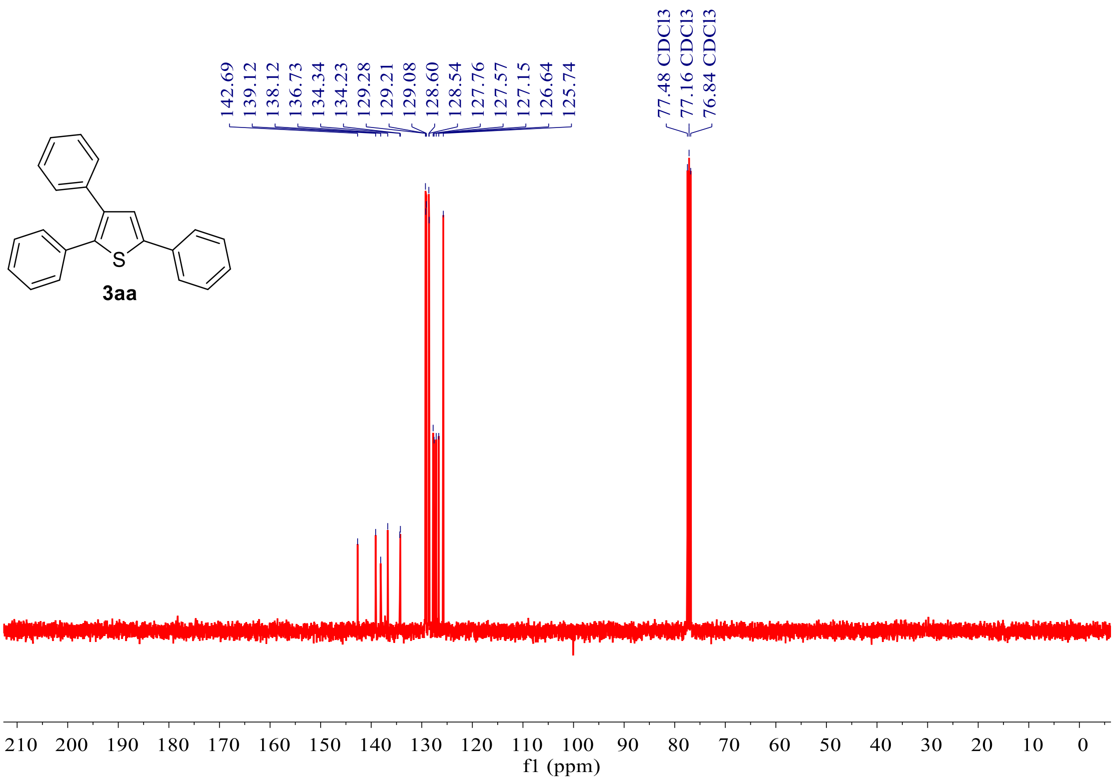
3al

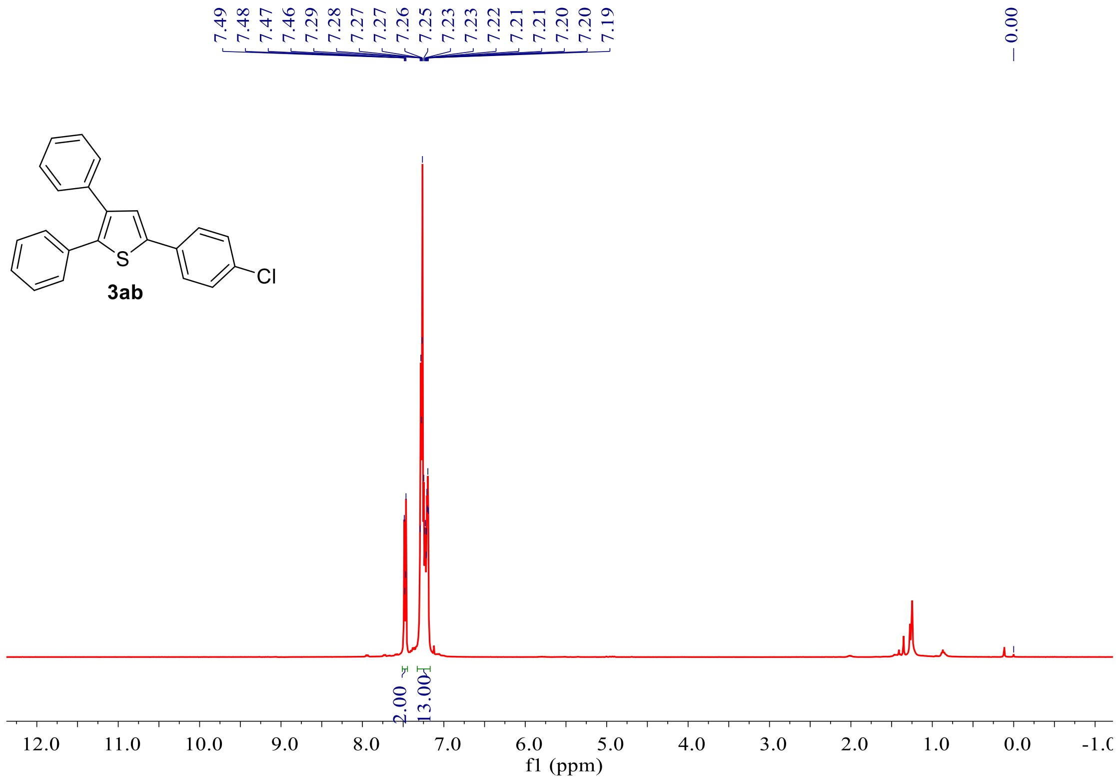


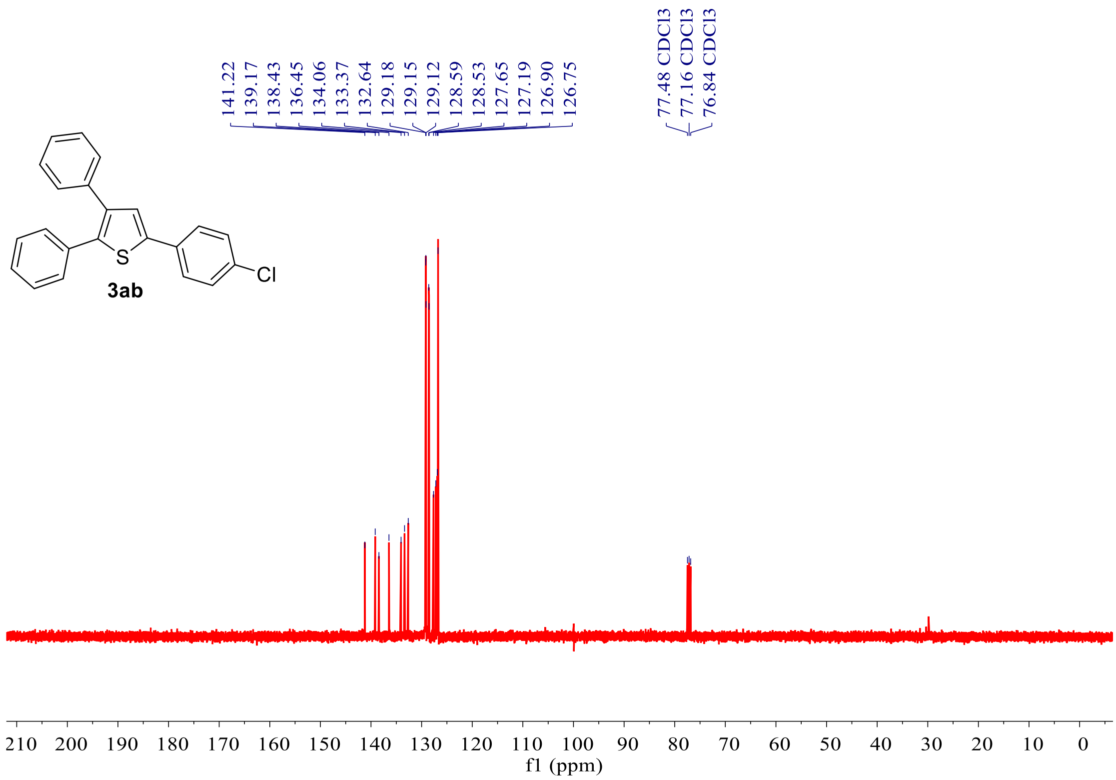
3am

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






7.49 7.48 7.47 7.46 7.29 7.28 7.27 7.27 7.26 7.25 7.23 7.23 7.22 7.21 7.21 7.20 7.20 7.19
0.00
S
Cl
3ab
2.00
13.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


141.22 139.17 138.43 136.45 134.06 133.37 132.64 129.18 129.15 129.12 128.59 128.53 127.65 127.19 126.90 126.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
S
Cl
3ab
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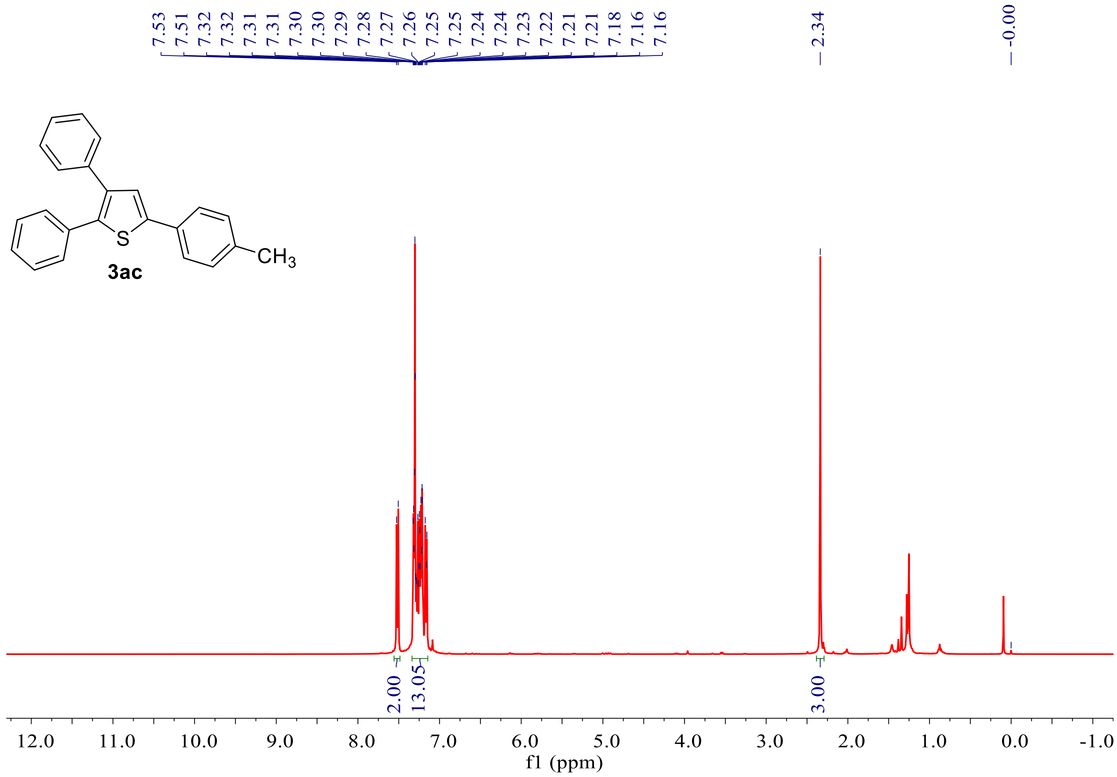
f1 (ppm)



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7.32
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7.29
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.21
7.21
7.18
7.16
7.16
2.34
-0.00
S
CH3
3ac
2.00
13.05
3.00
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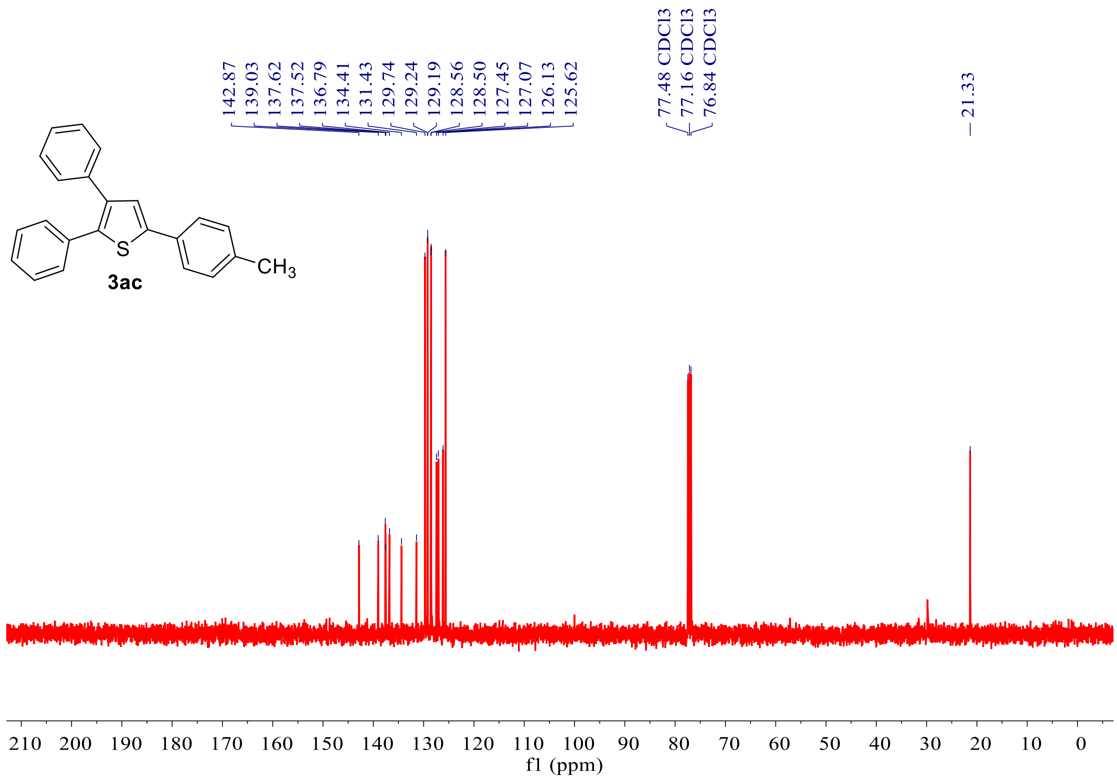
f1 (ppm)



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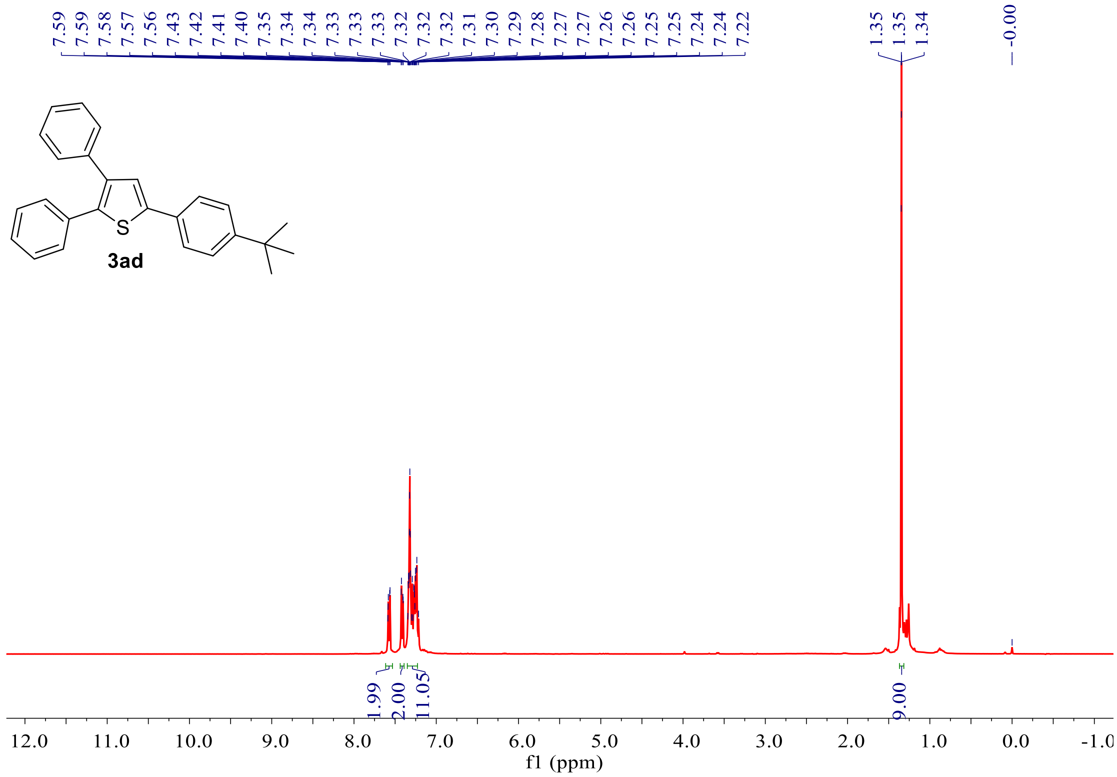
127.45
127.07
126.13
125.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.33
S
CH3
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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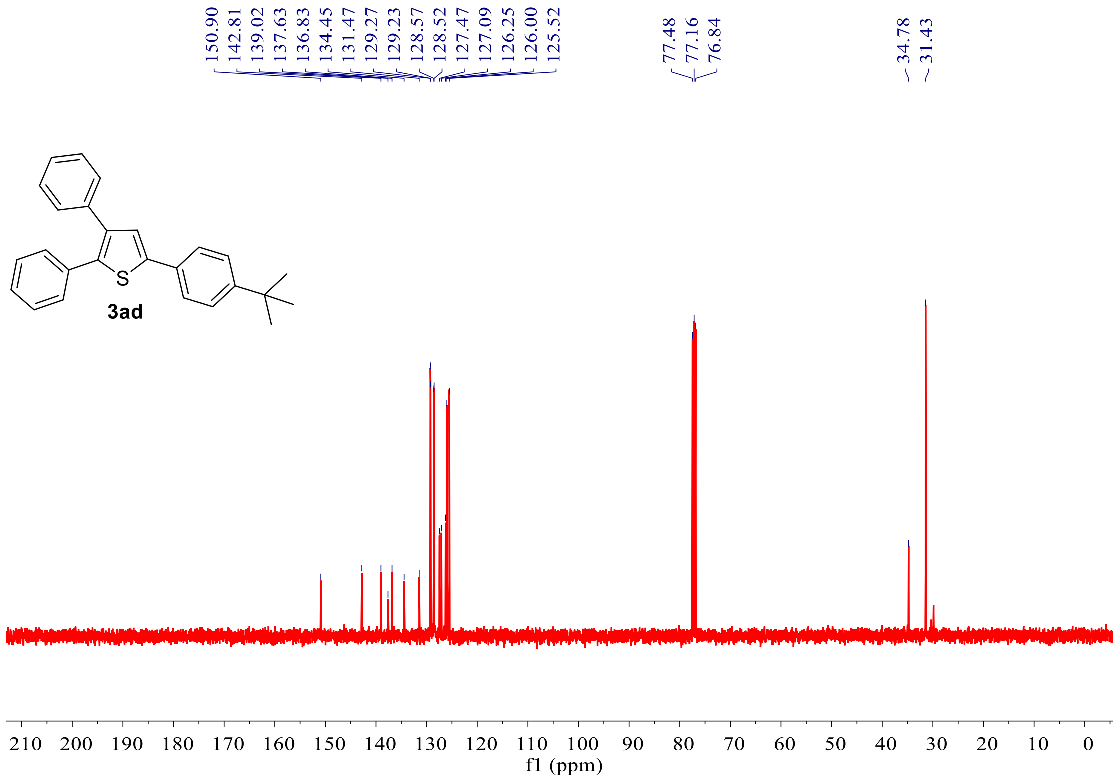
1.35 1.35 1.34
-0.00
S
3ad
1.99 2.00 11.05
9.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


150.90 142.81 139.02 137.63 136.83 134.45 131.47 129.27 129.23 128.57 128.52 127.47 127.09 126.25 126.00 125.52
77.48 77.16 76.84
34.78 31.43
S
3ad
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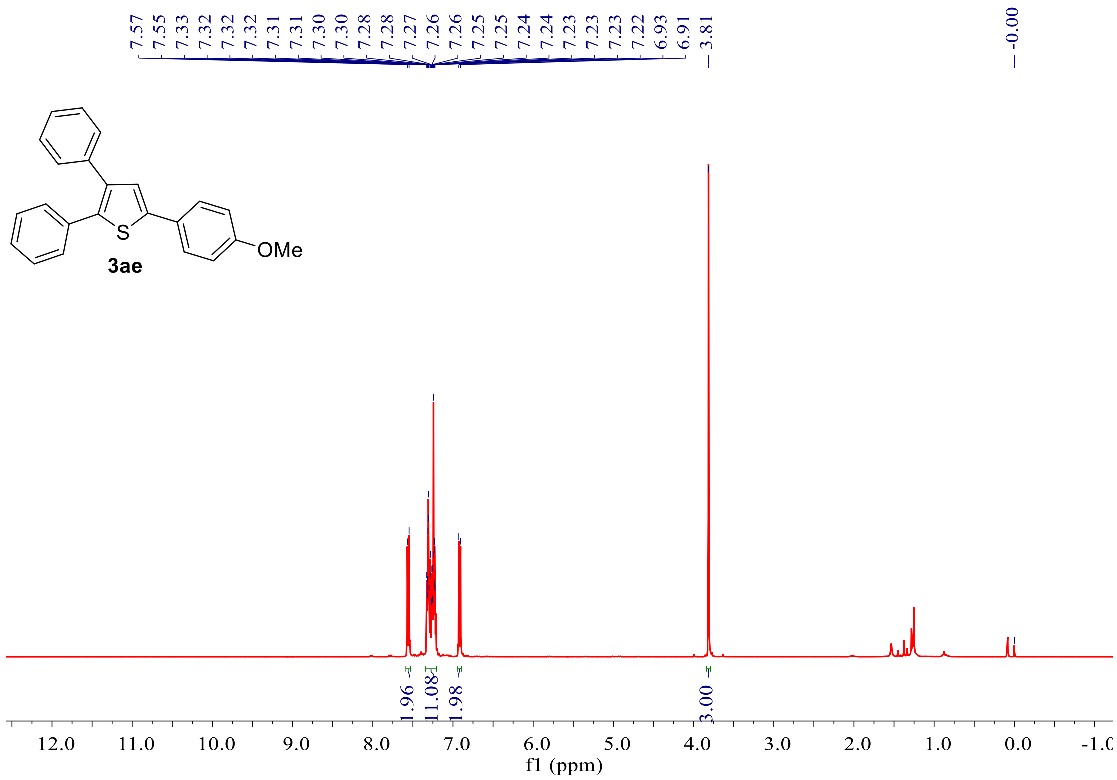
f1 (ppm)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7.22
6.93
6.91
3.81
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OMe
S
3ae
1.96
11.08
1.98
3.00
12.0
11.0
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5.0
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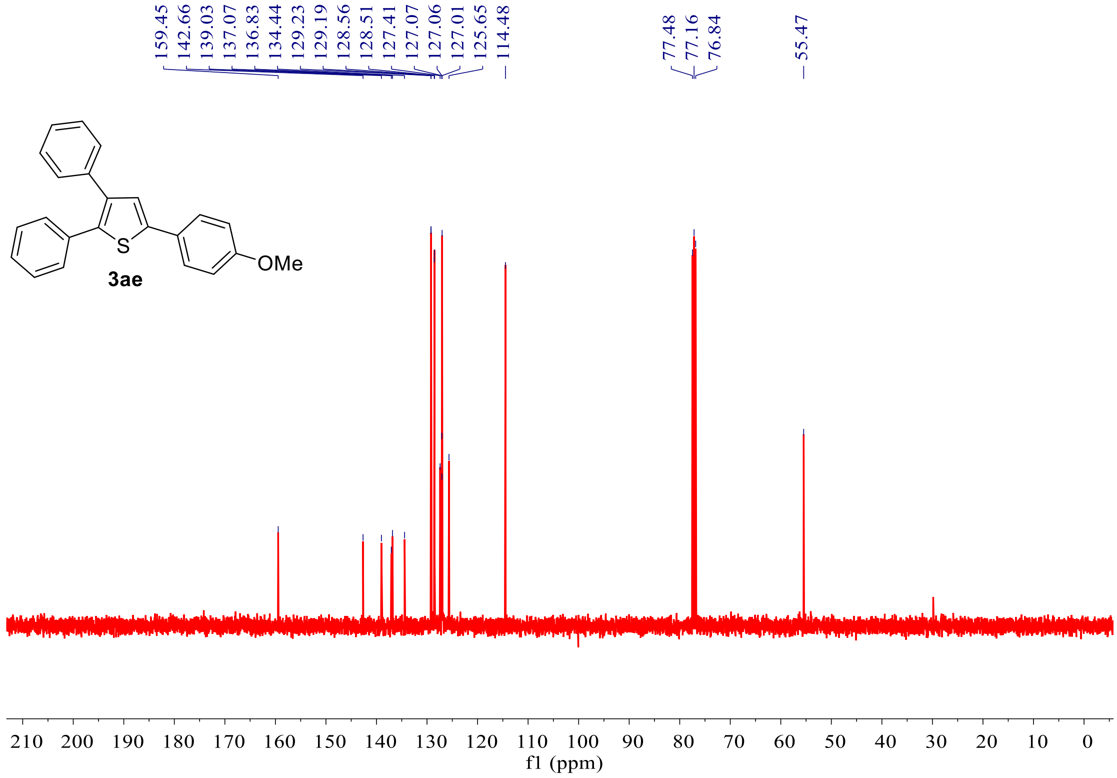
2.0
1.0
0.0
f1 (ppm)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127.06
127.01
125.65
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77.16
76.84
55.47
OMe
S
3ae
210
200
190
180
170
160
150
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130
120
110
100
90
80
70
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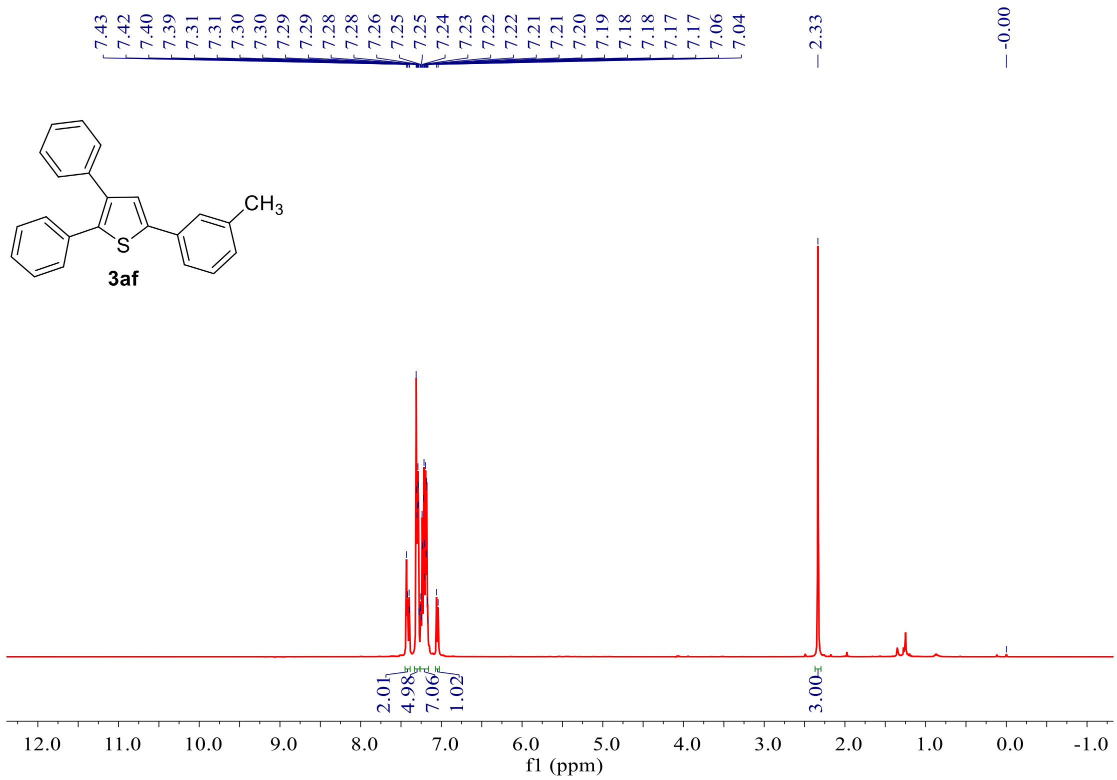
50
40
30
20
10
0
f1 (ppm)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7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.17
7.06
7.04
2.33
-0.00
CH3
S
3af
2.01
4.98
7.06
1.02
3.00
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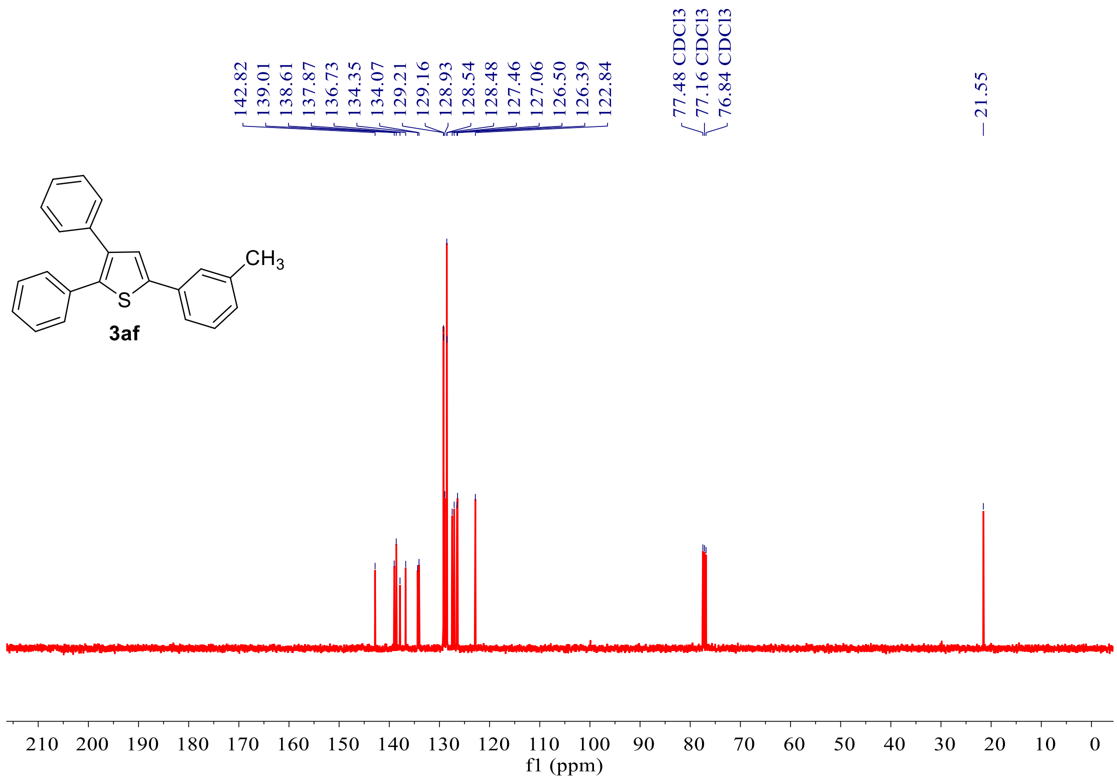
f1 (ppm)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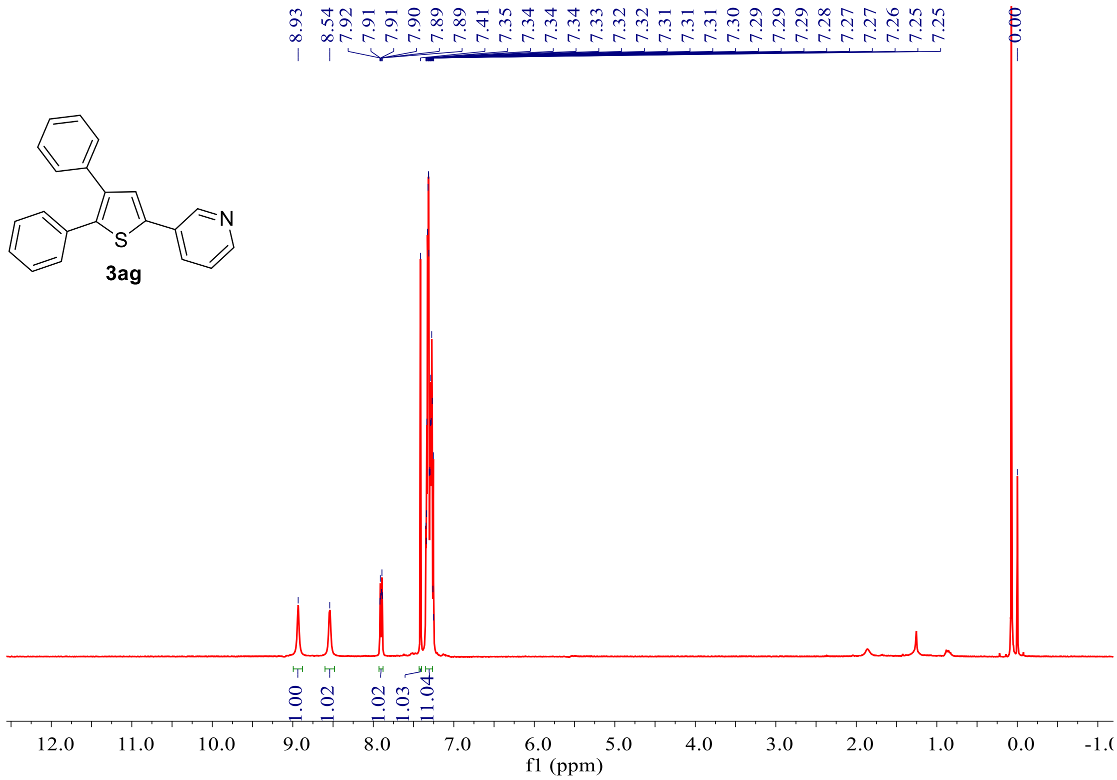
127.06
126.50
126.39
122.84
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.55
CH3
S
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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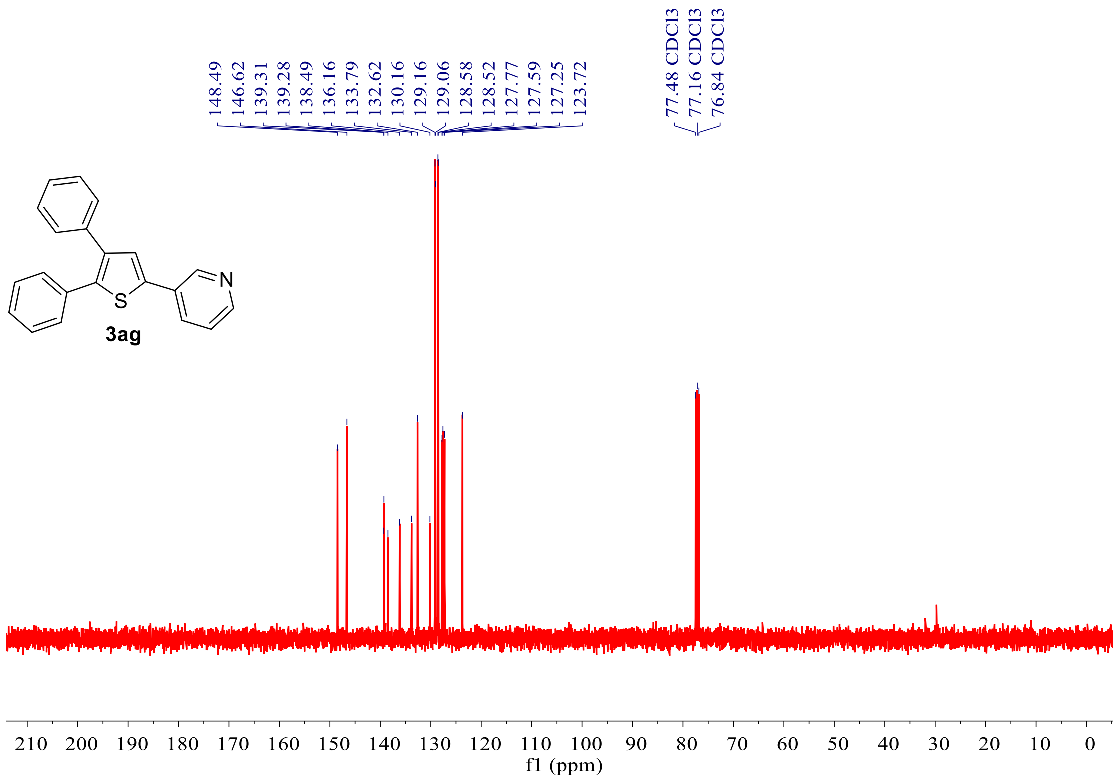
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
0.00
S
N
3ag
1.00
1.02
1.02
1.03
11.04
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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132.62
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129.16
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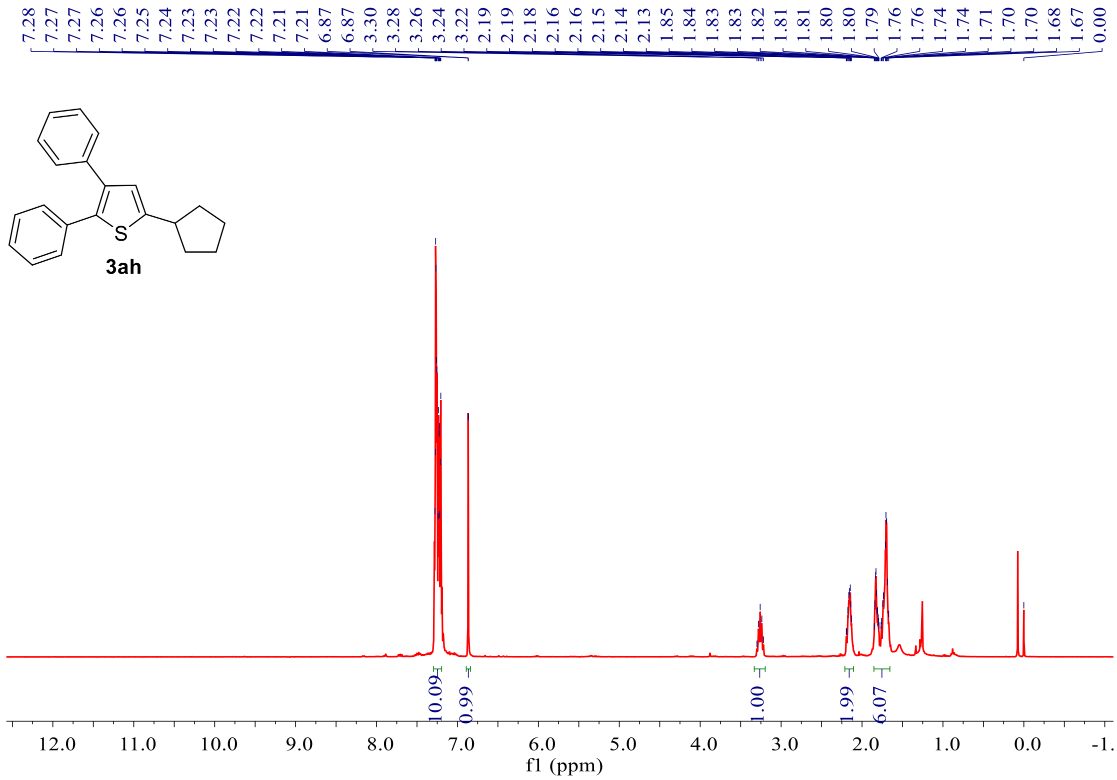
128.52
127.77
127.59
127.25
123.72
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
S
N
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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S
3ah
10.09
0.99
1.00
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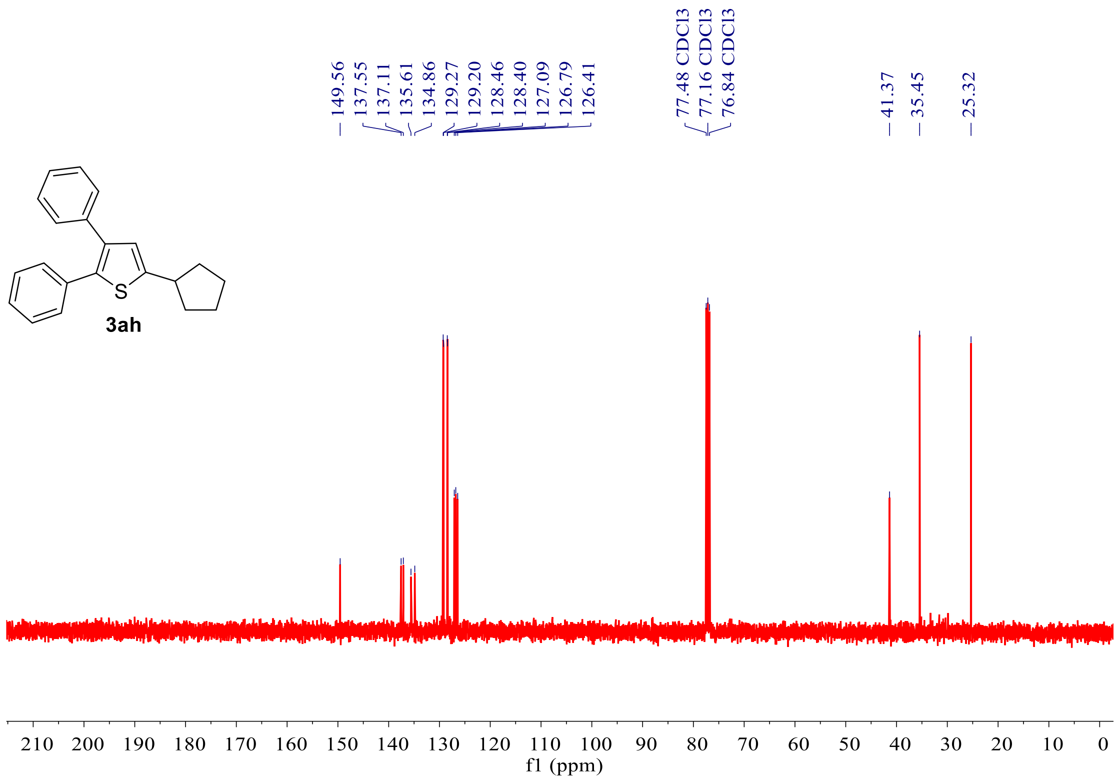
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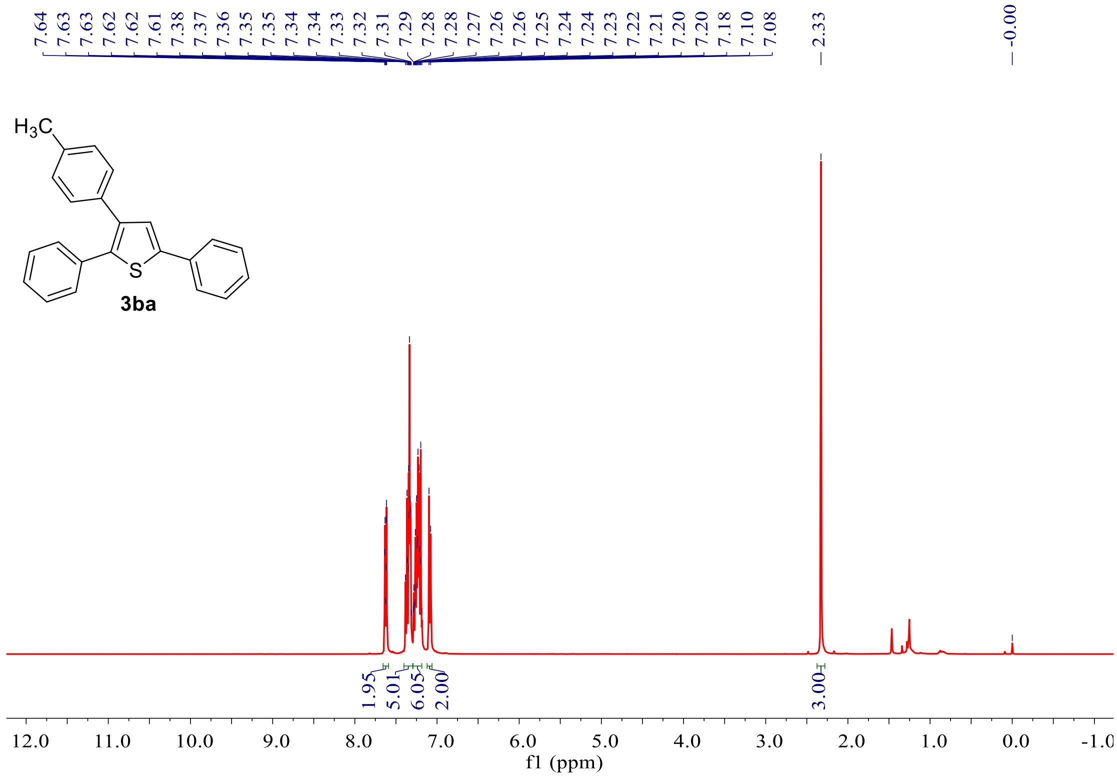
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7.20
7.18
7.10
7.08
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S
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5.01
6.05
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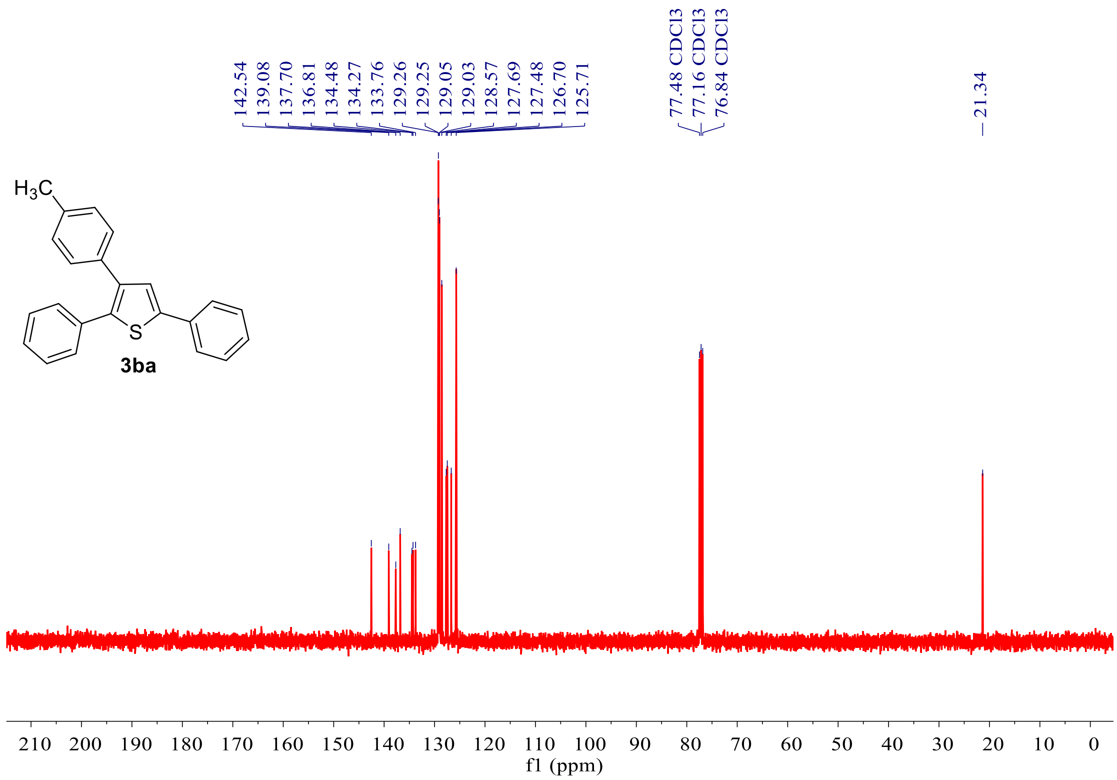
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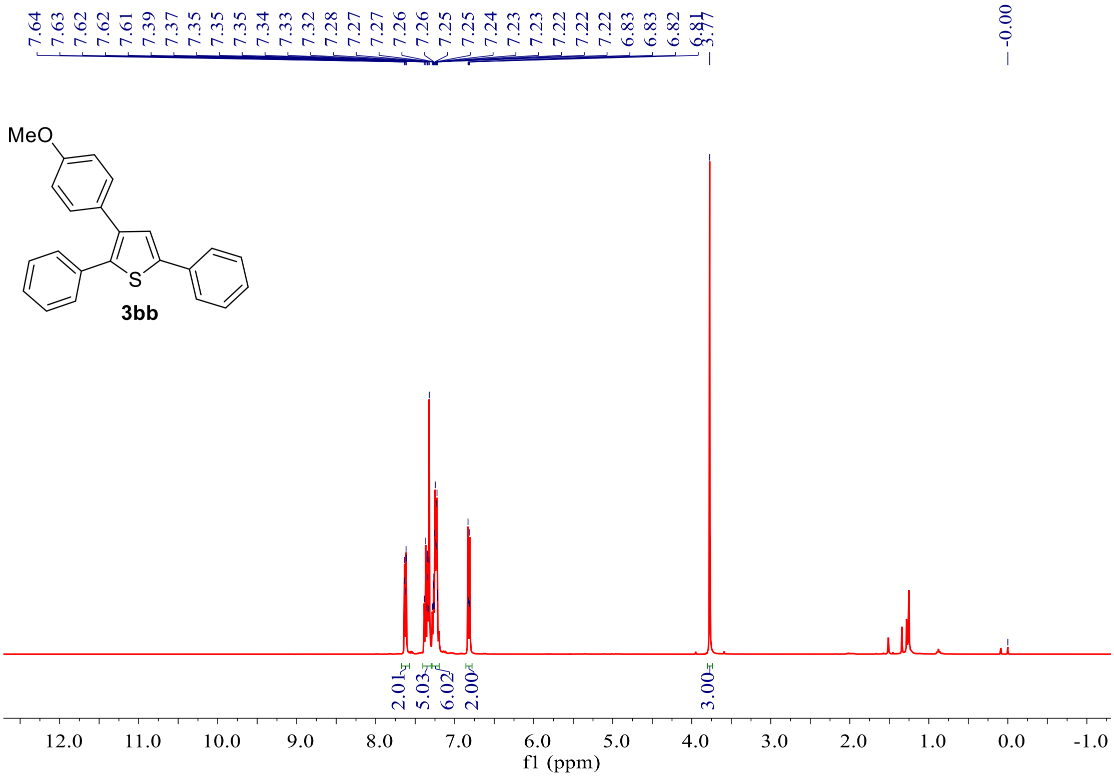
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-0.00
MeO
S
3bb
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5.03
6.02
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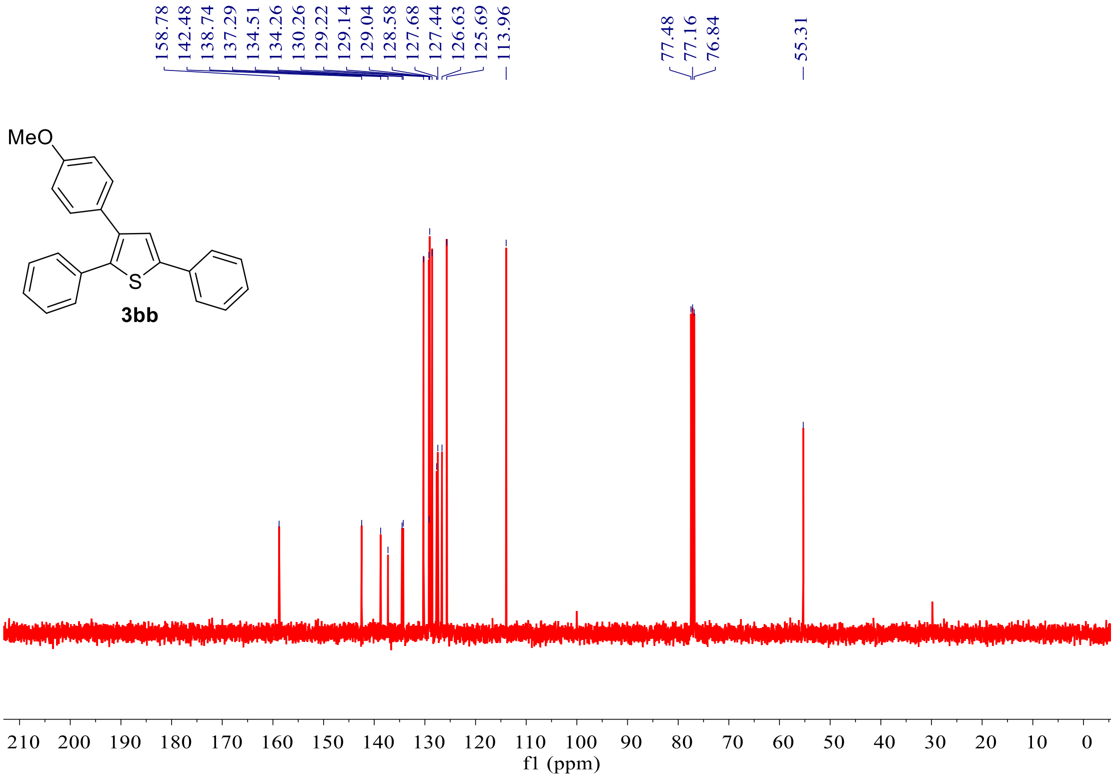
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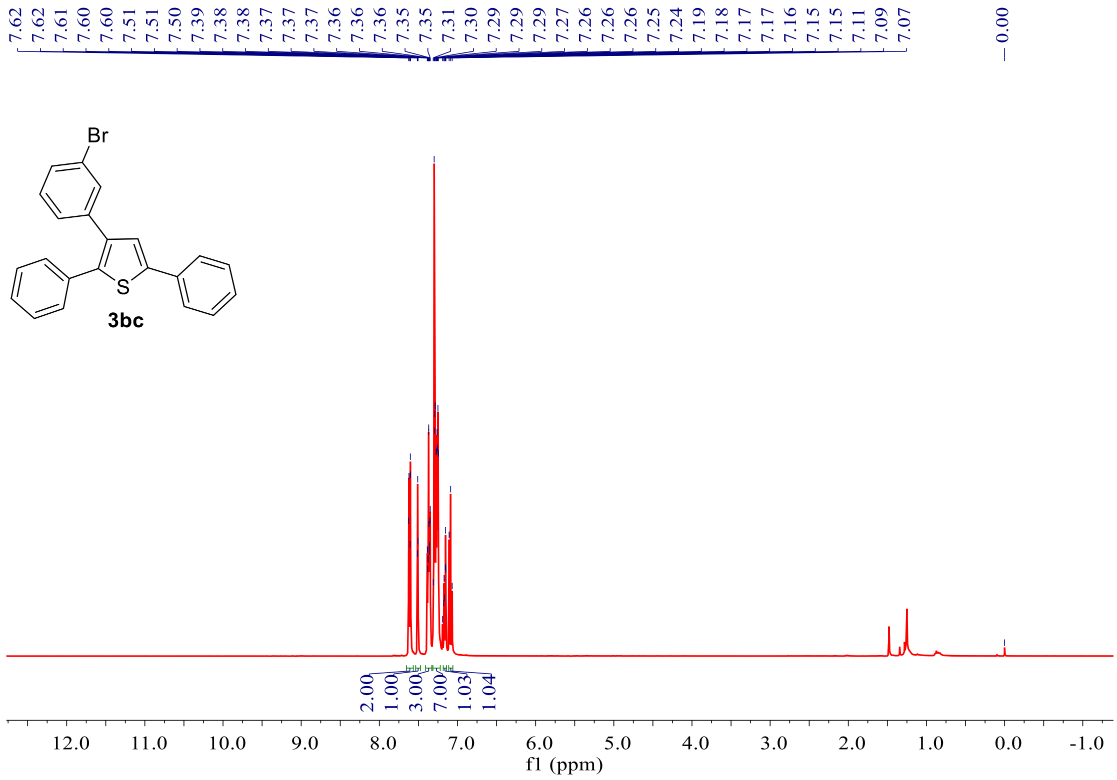
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3bc
2.00 1.00 3.00 7.00 1.03 1.04
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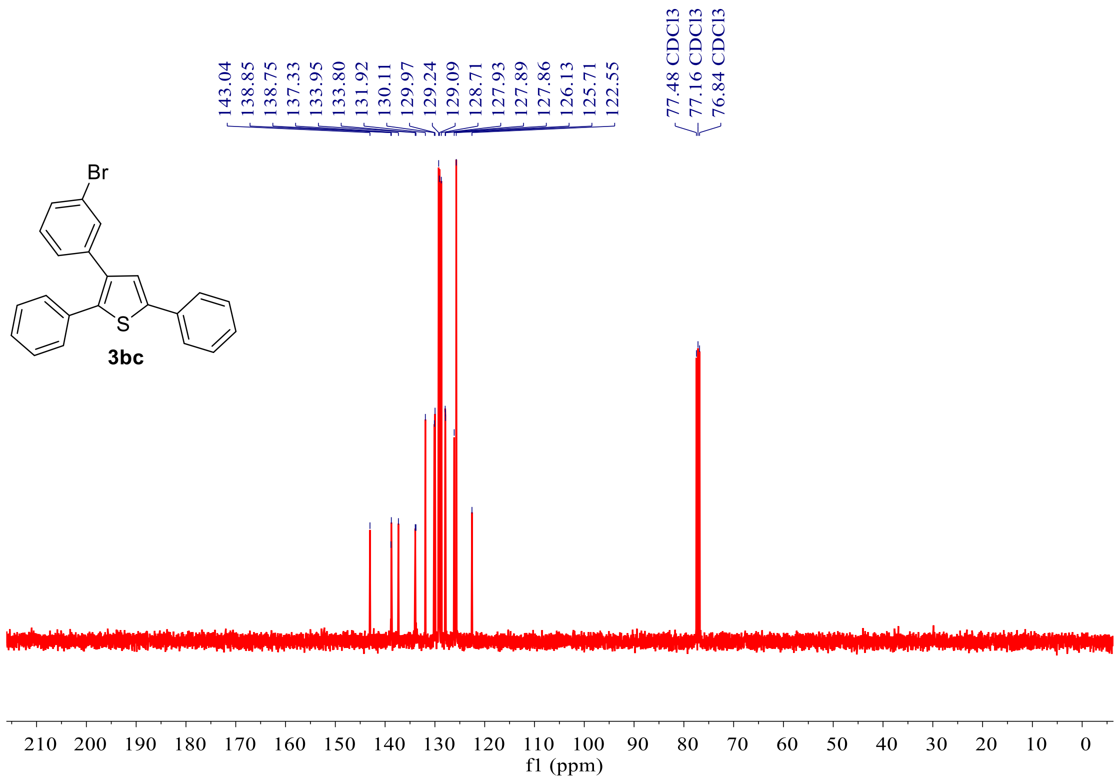
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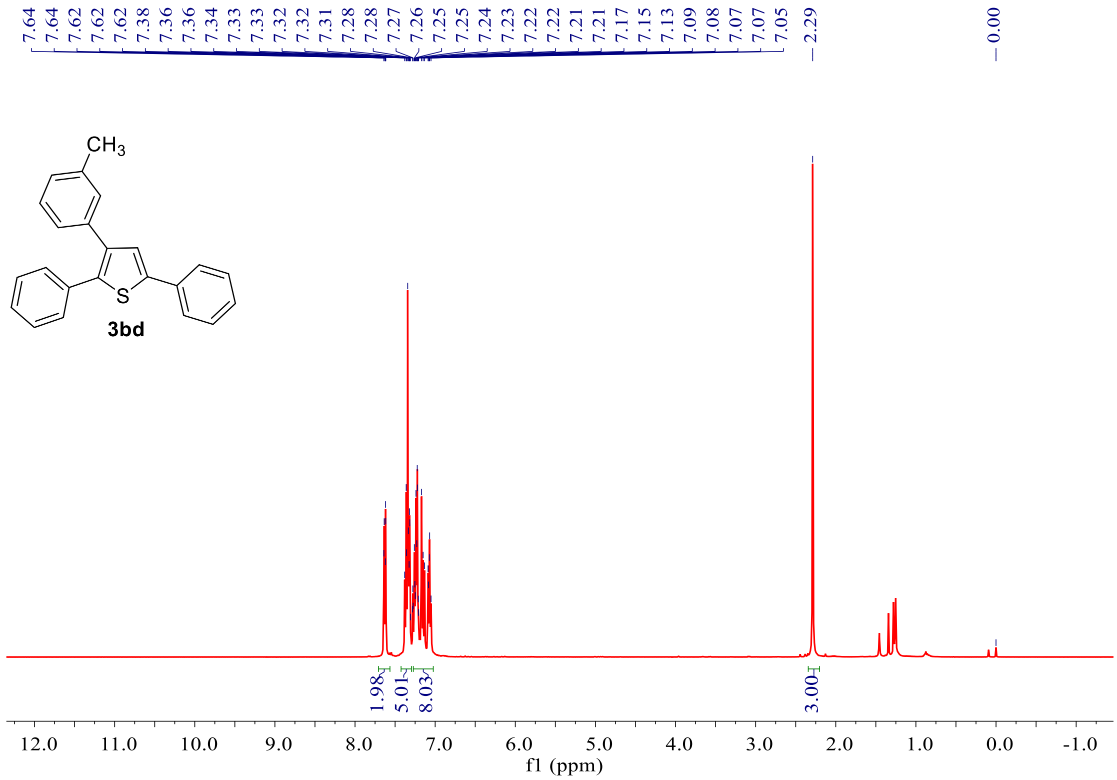
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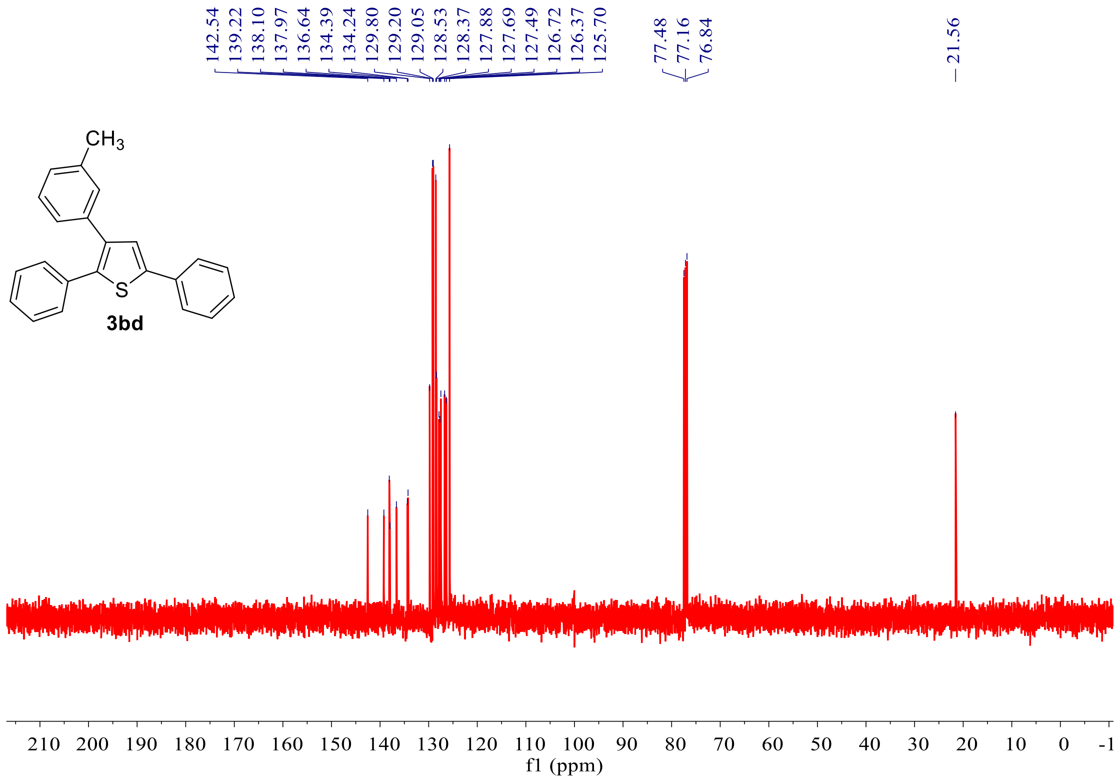
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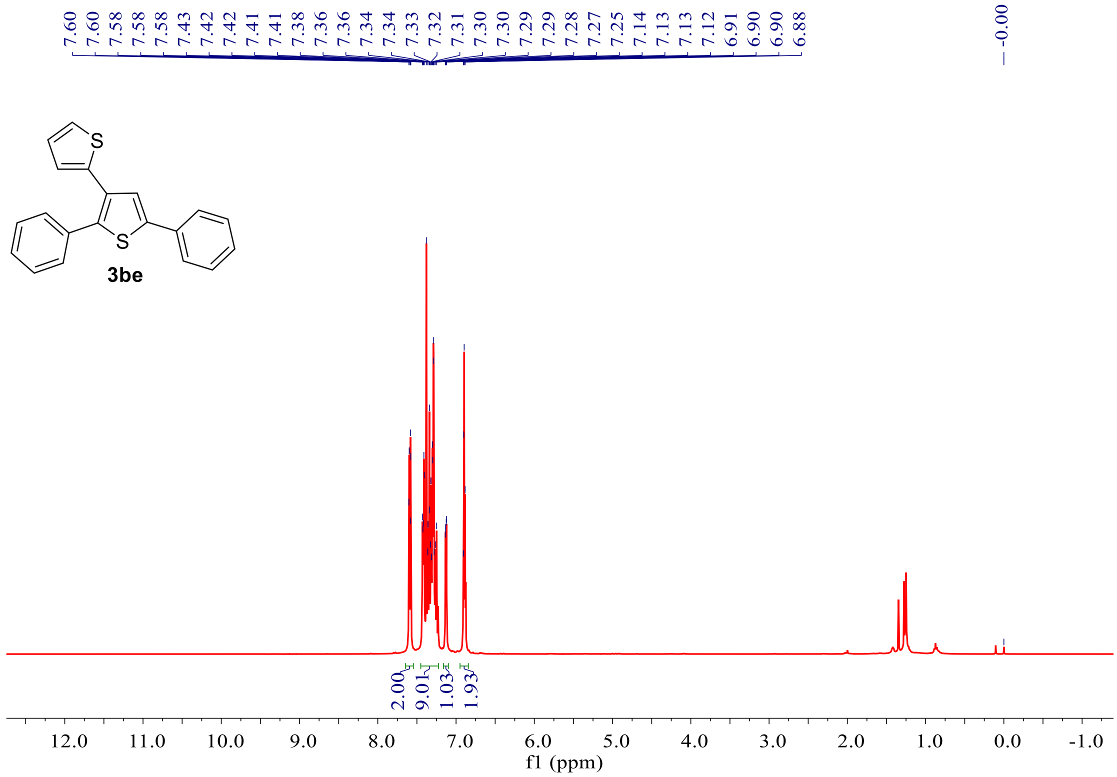
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6.88
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2.00
9.01
1.03
1.93
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10.0
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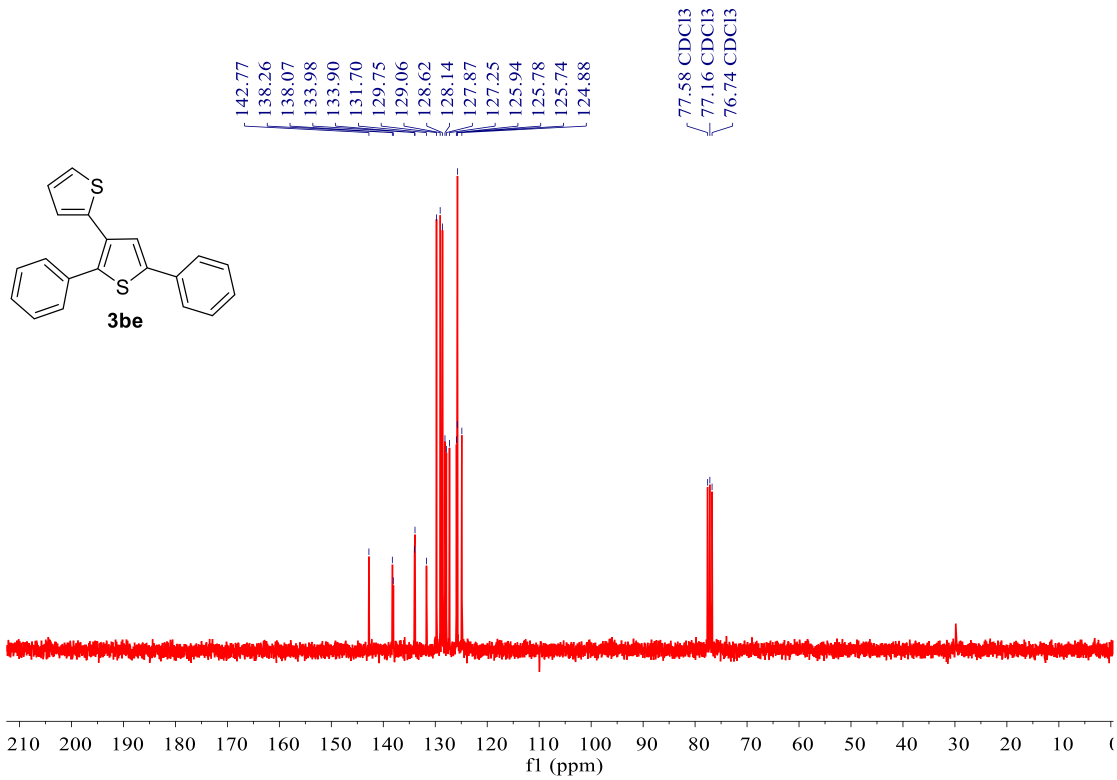
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76.74 CDCl3
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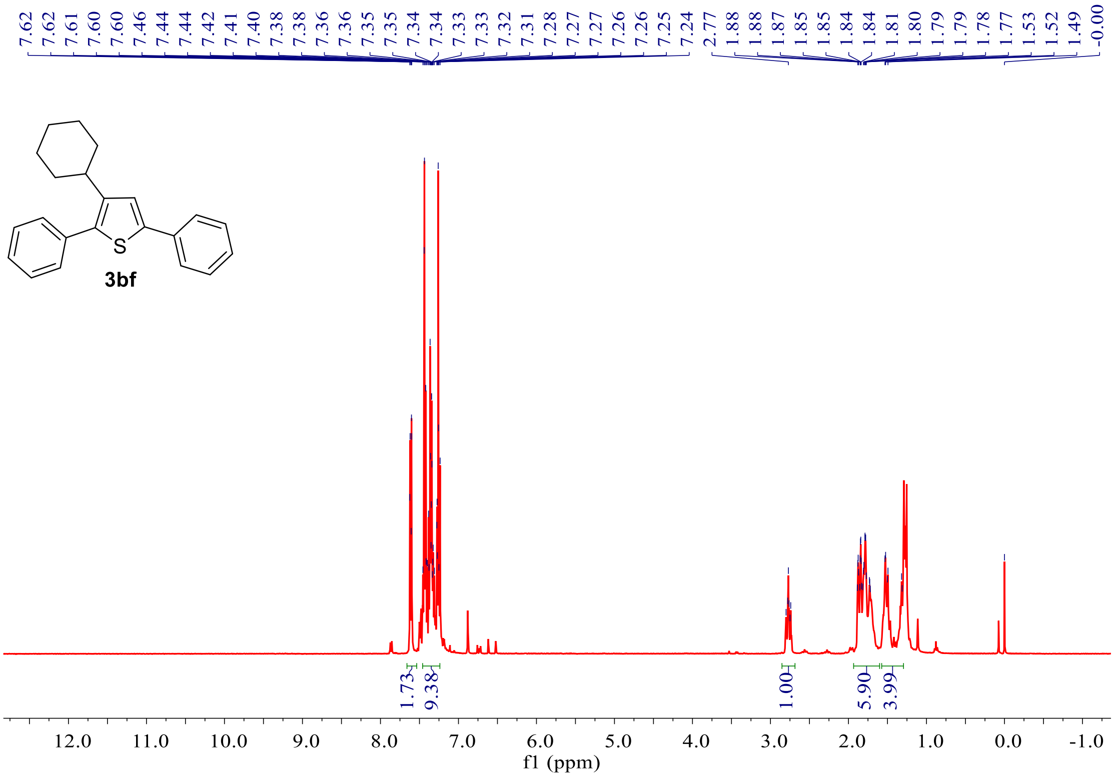
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1.81
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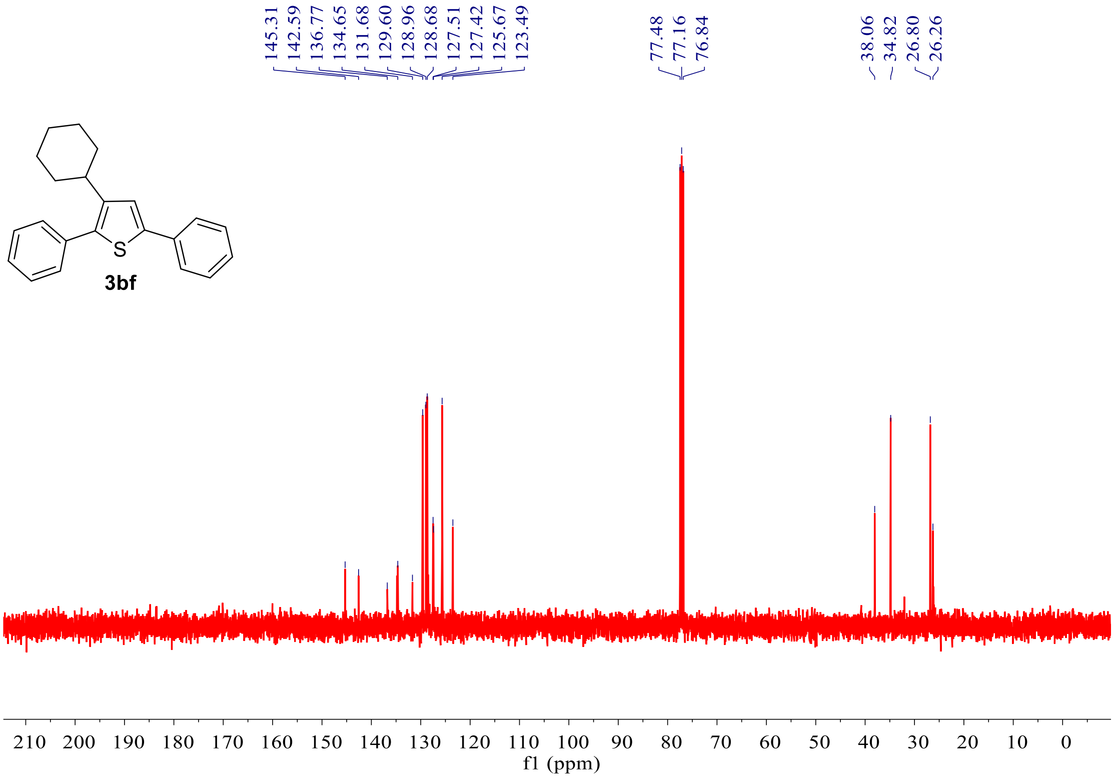
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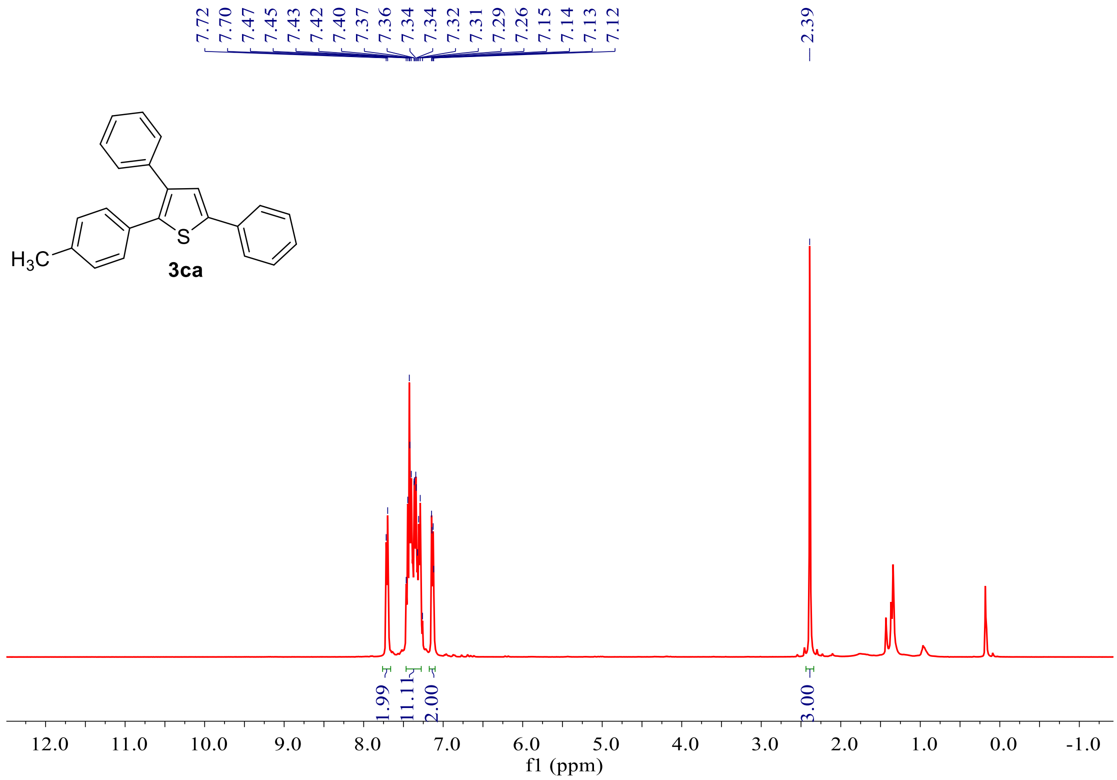
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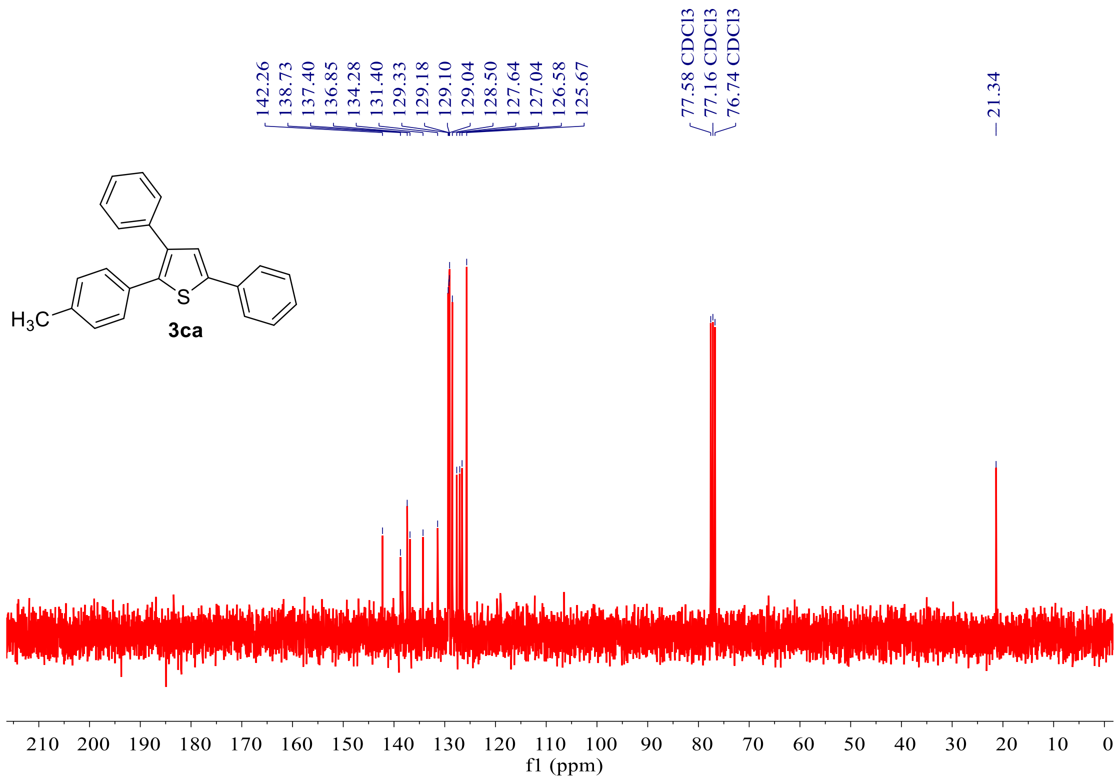
f1 (ppm)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125.67
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
21.34
H3C
S
3ca
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200
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180
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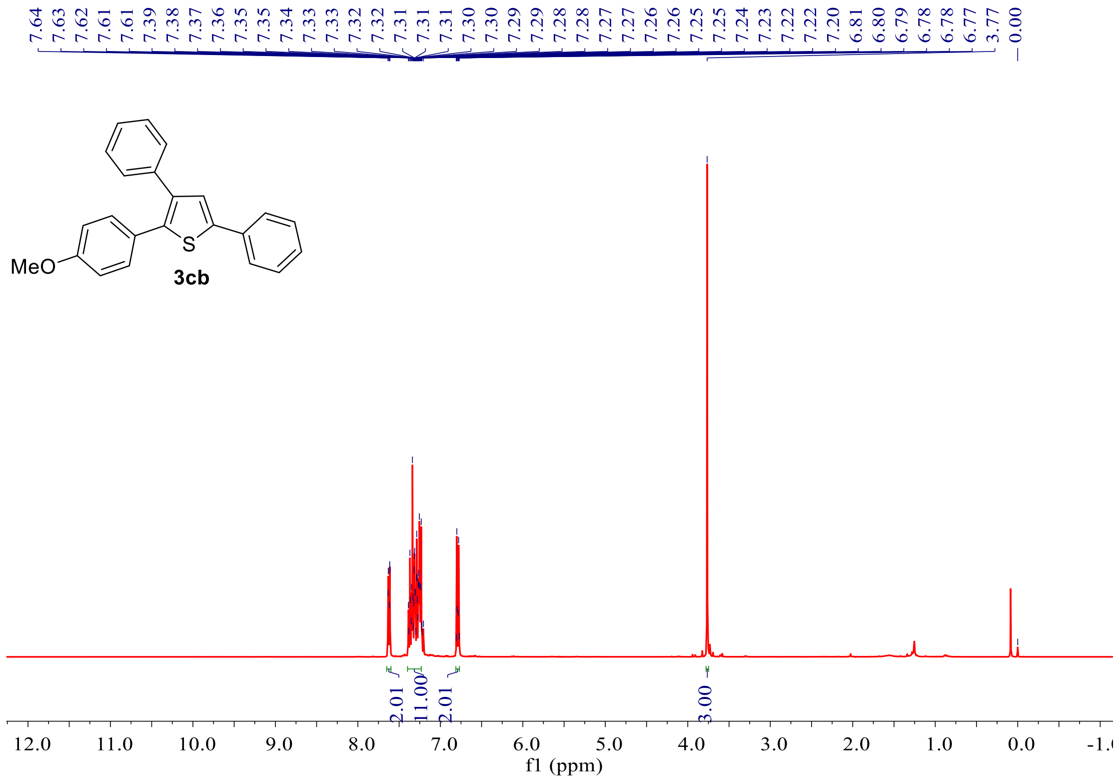
f1 (ppm)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0.00
MeO
S
3cb
2.01
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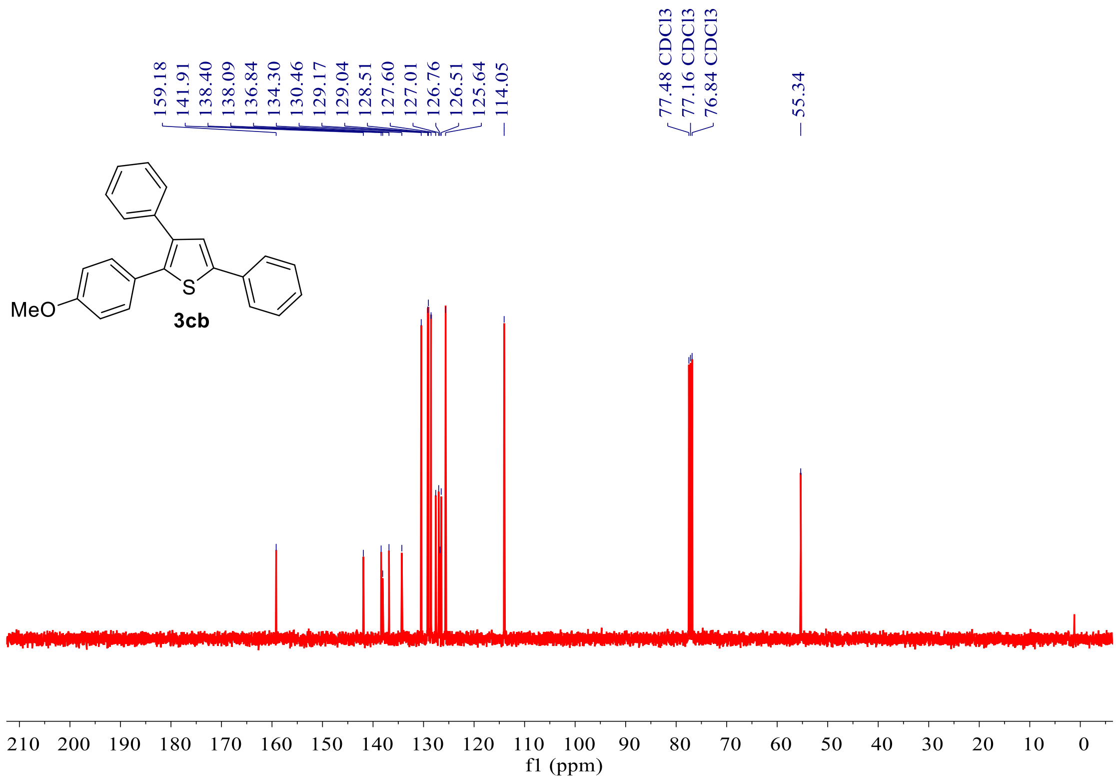
f1 (ppm)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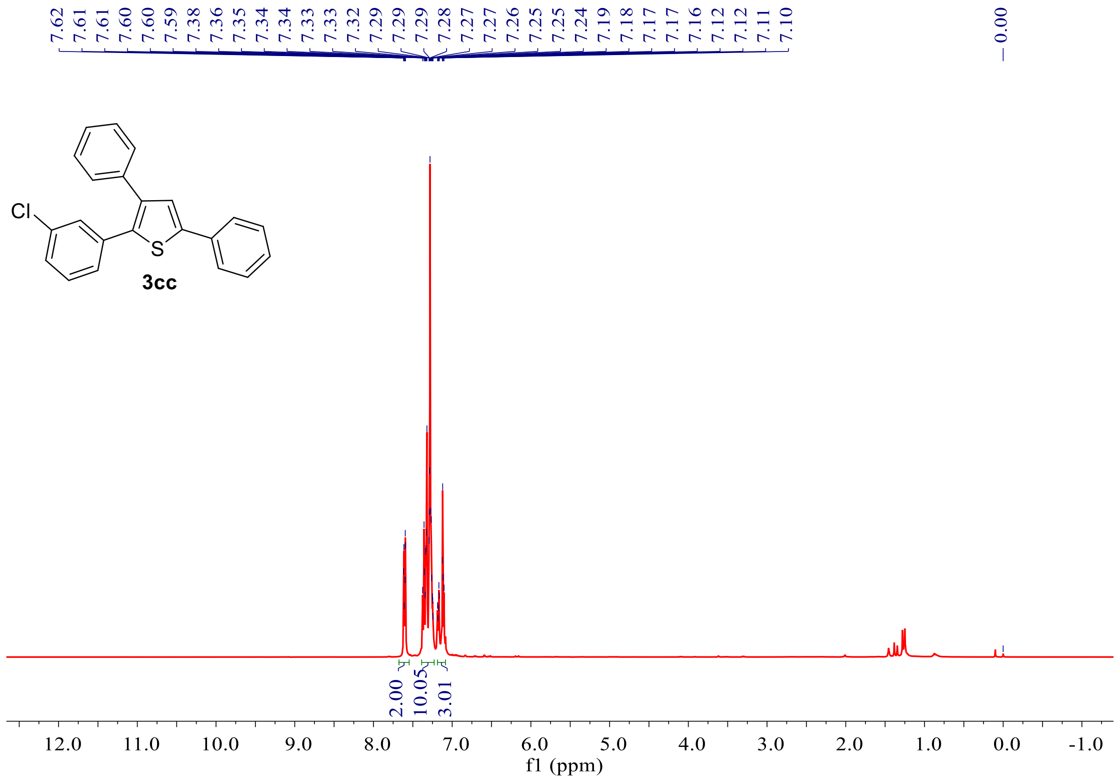
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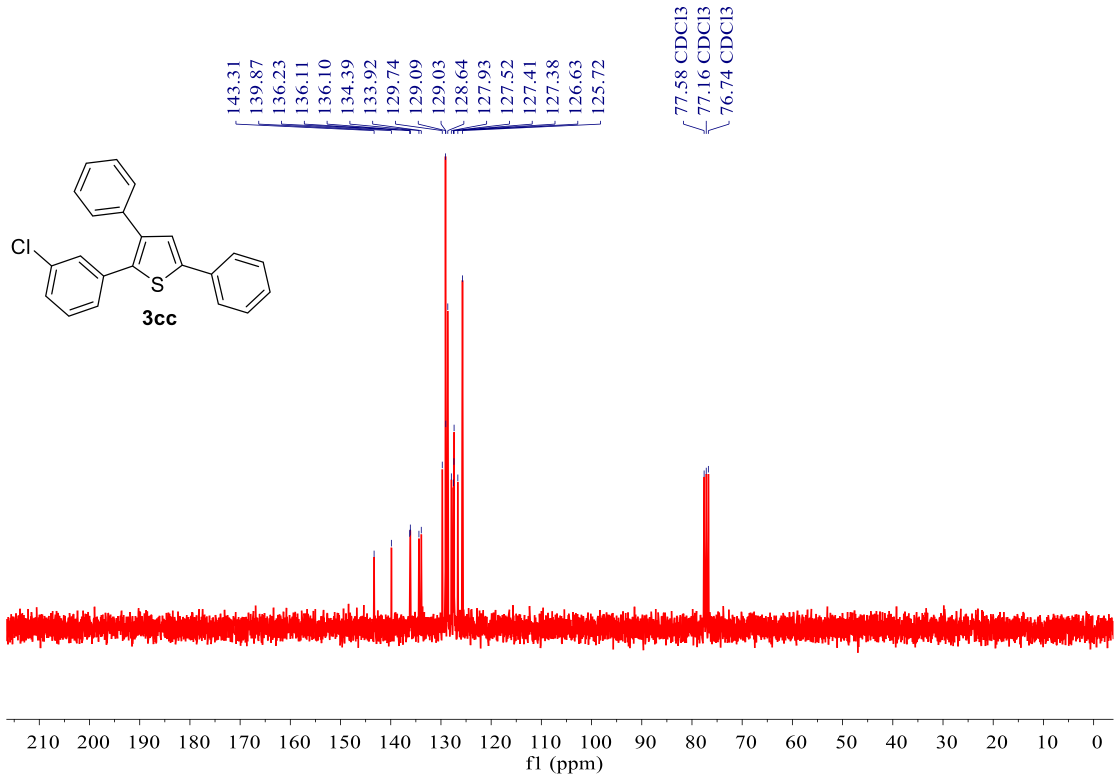
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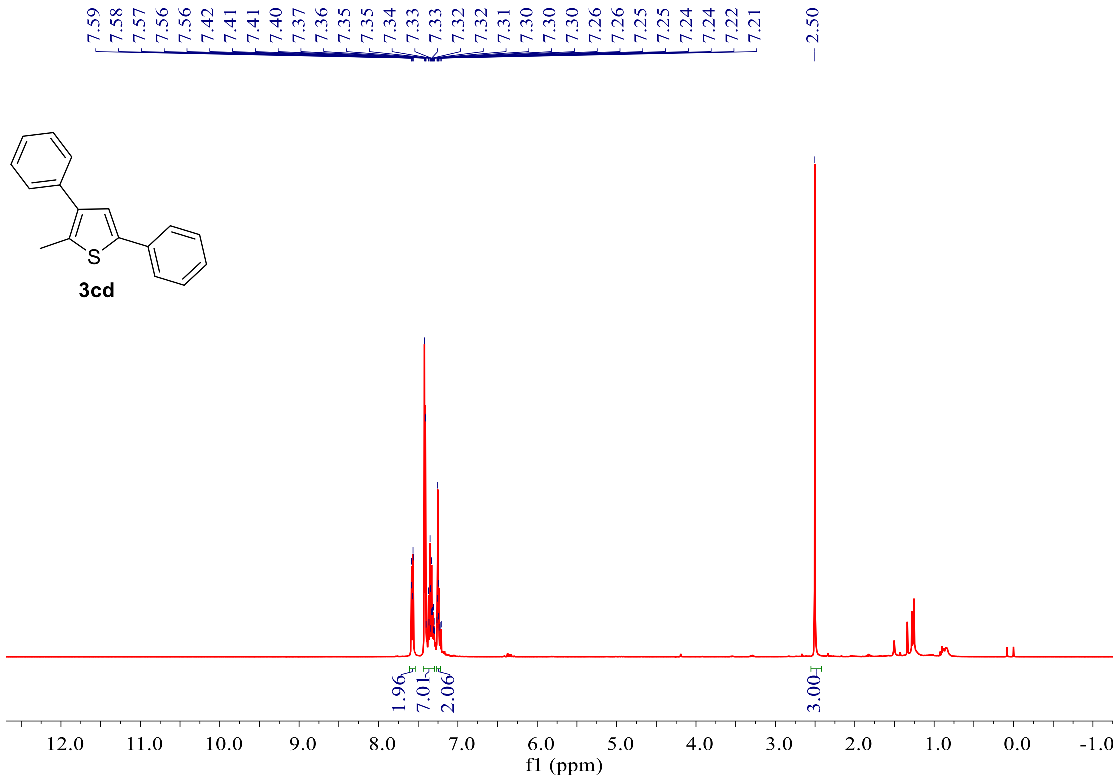
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2.50
S
3cd
1.96
7.01
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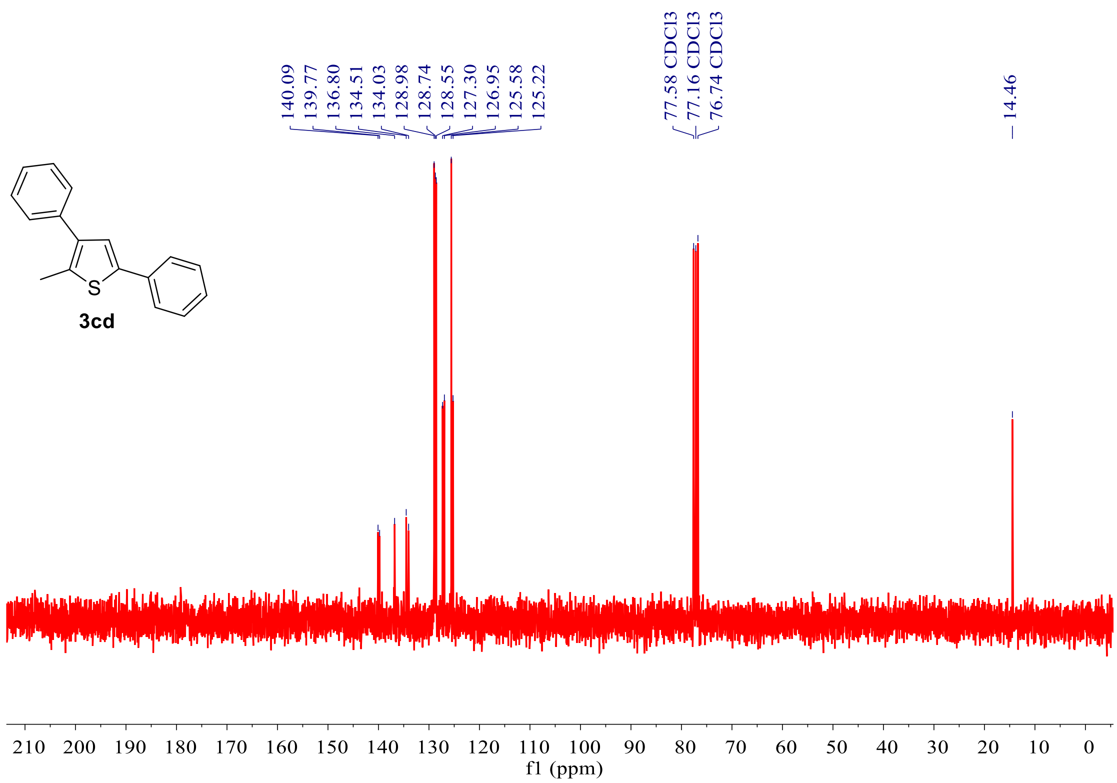
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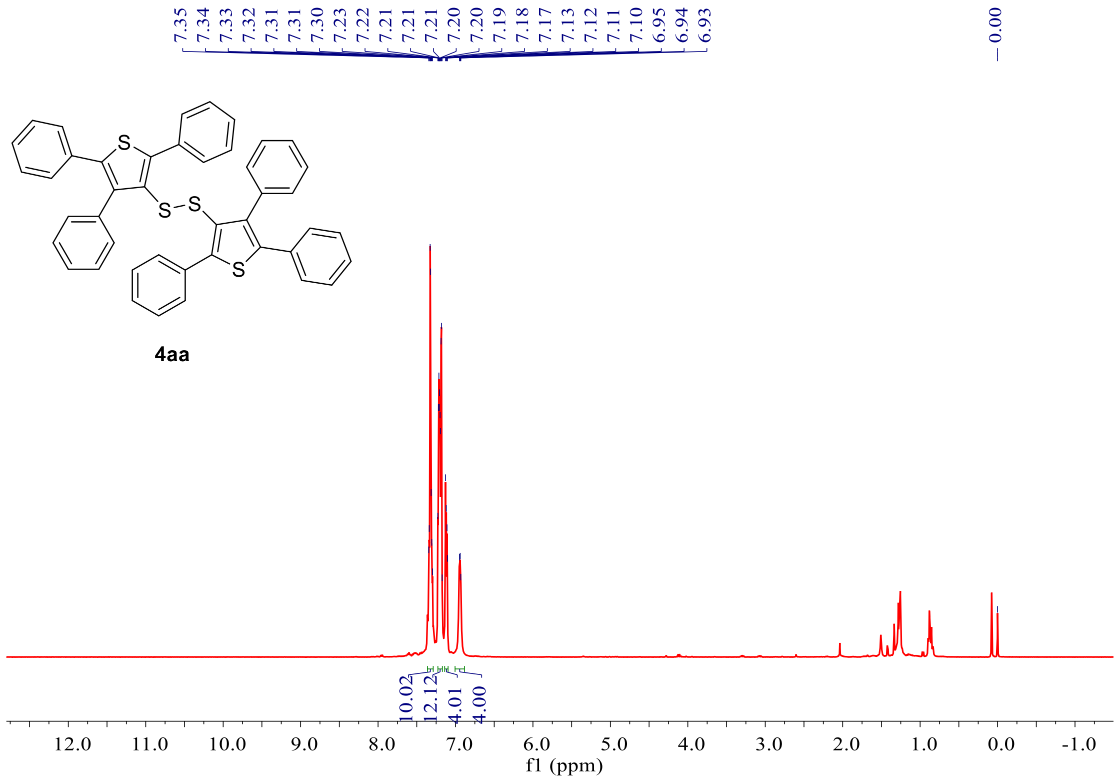
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S
S
S
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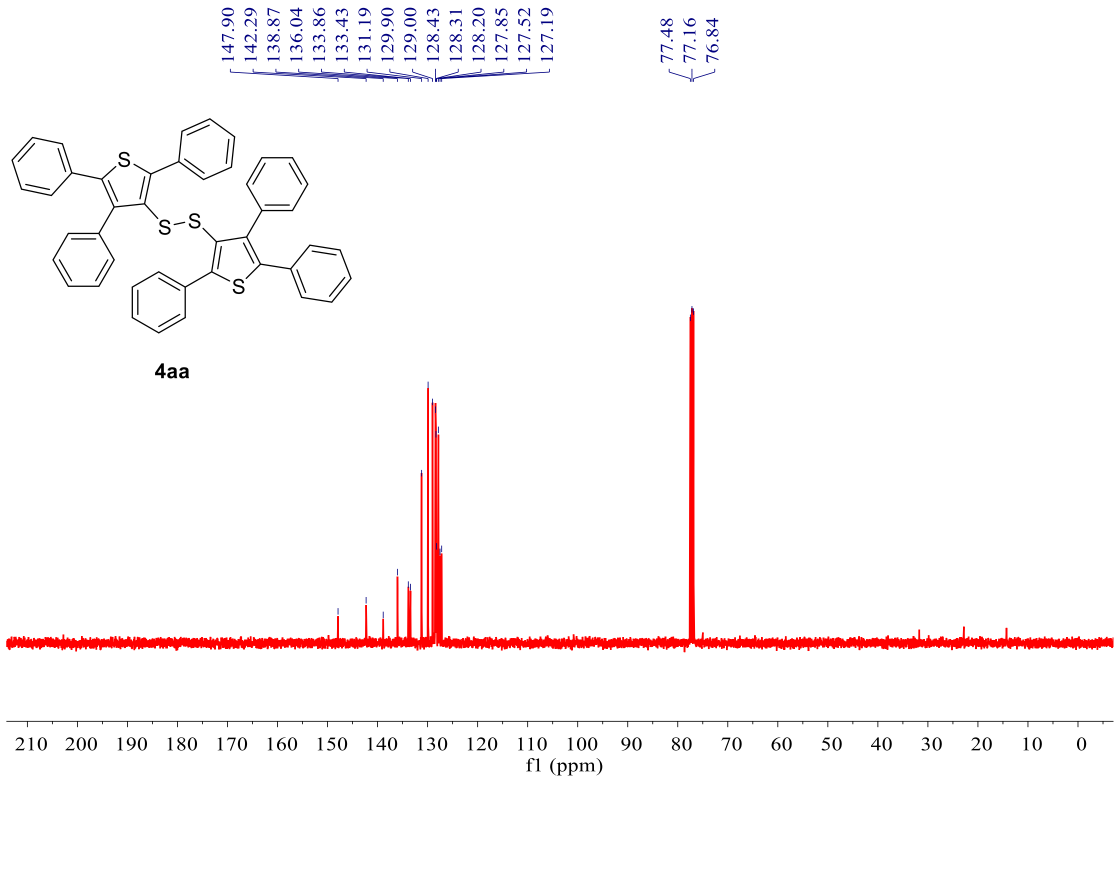
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S
S
S
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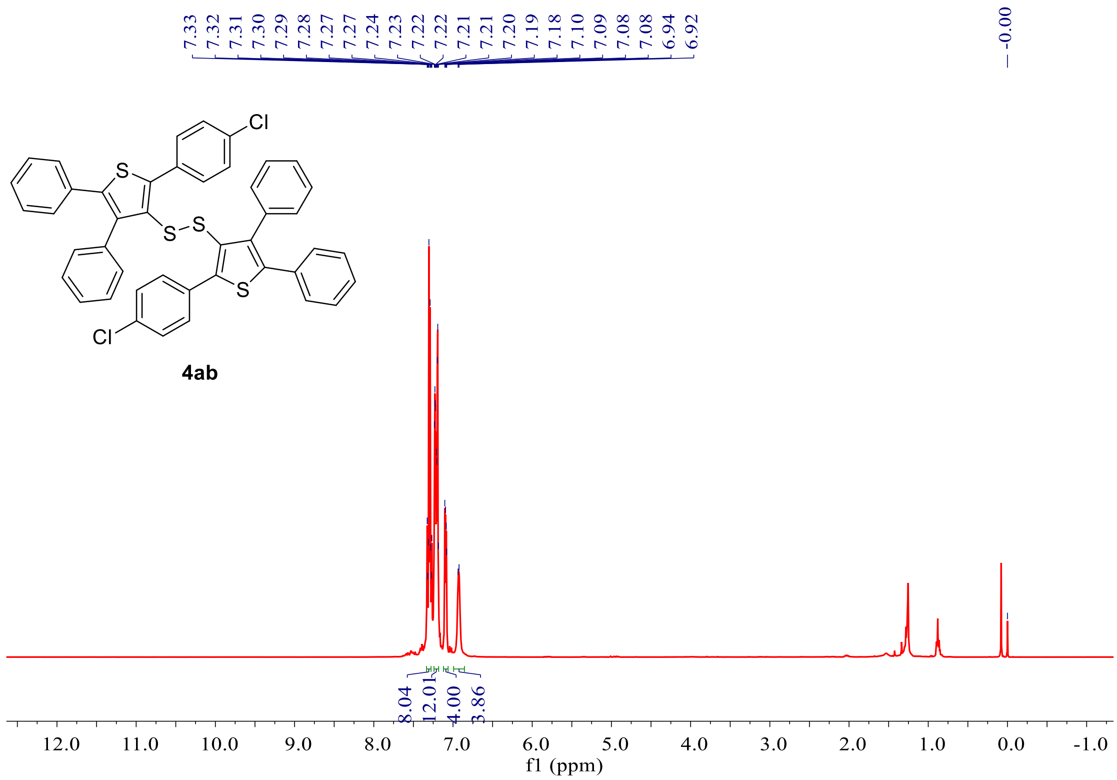
f1 (ppm)



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7.08
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S
S
S
S
Cl
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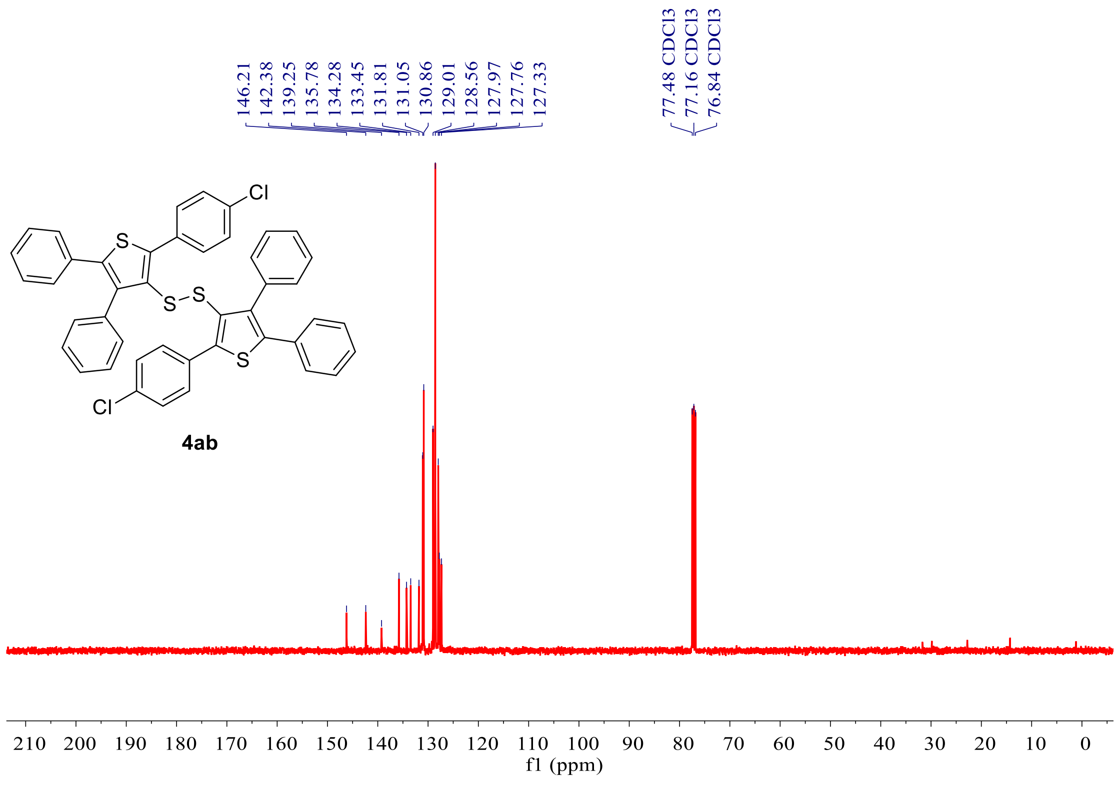
f1 (ppm)



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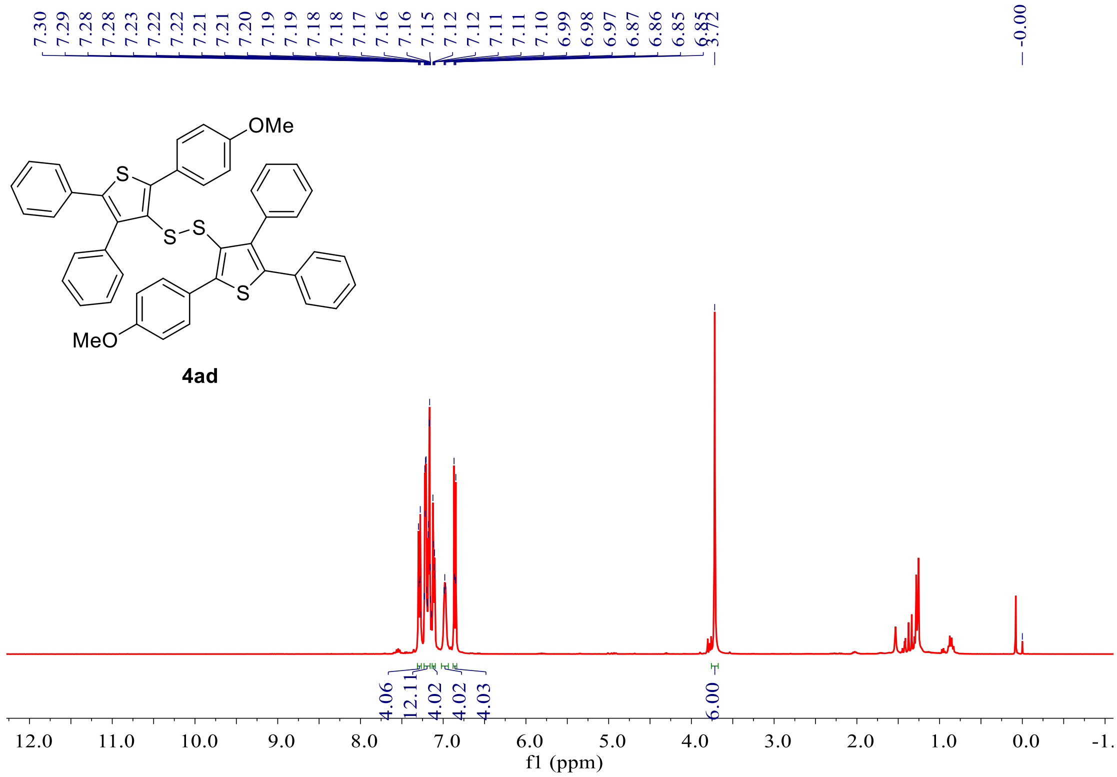
f1 (ppm)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6.00
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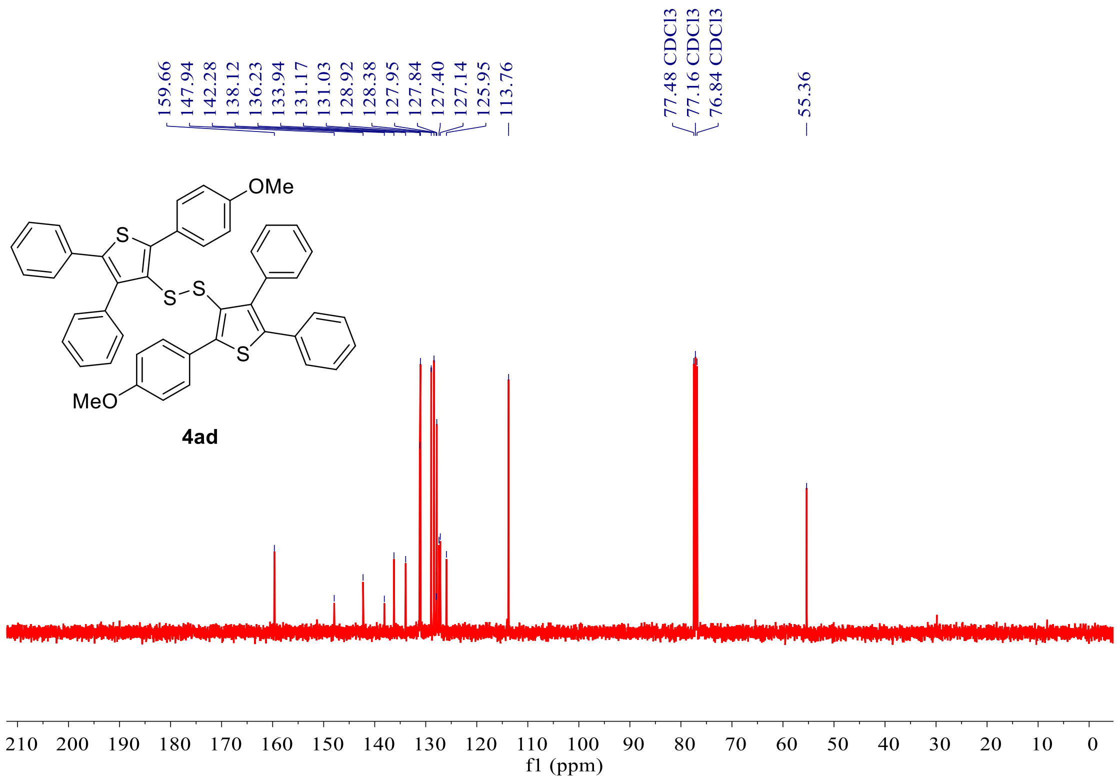
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76.84 CDCl3
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OMe
MeO
S
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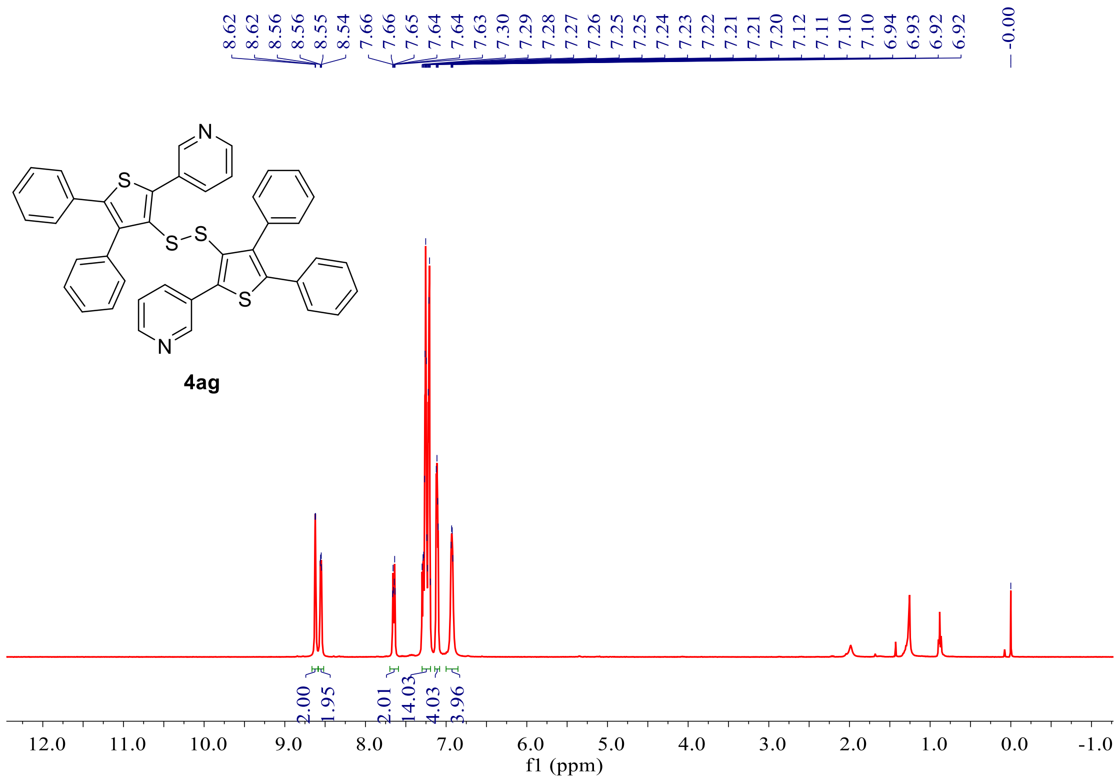
f1 (ppm)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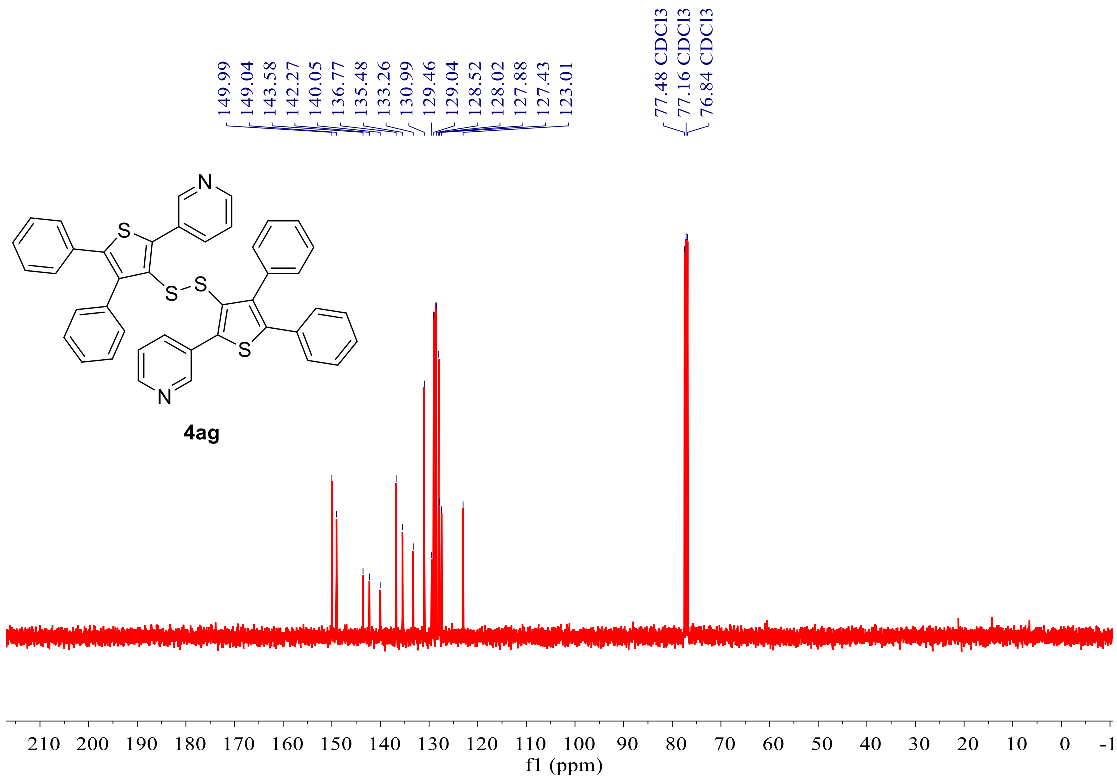
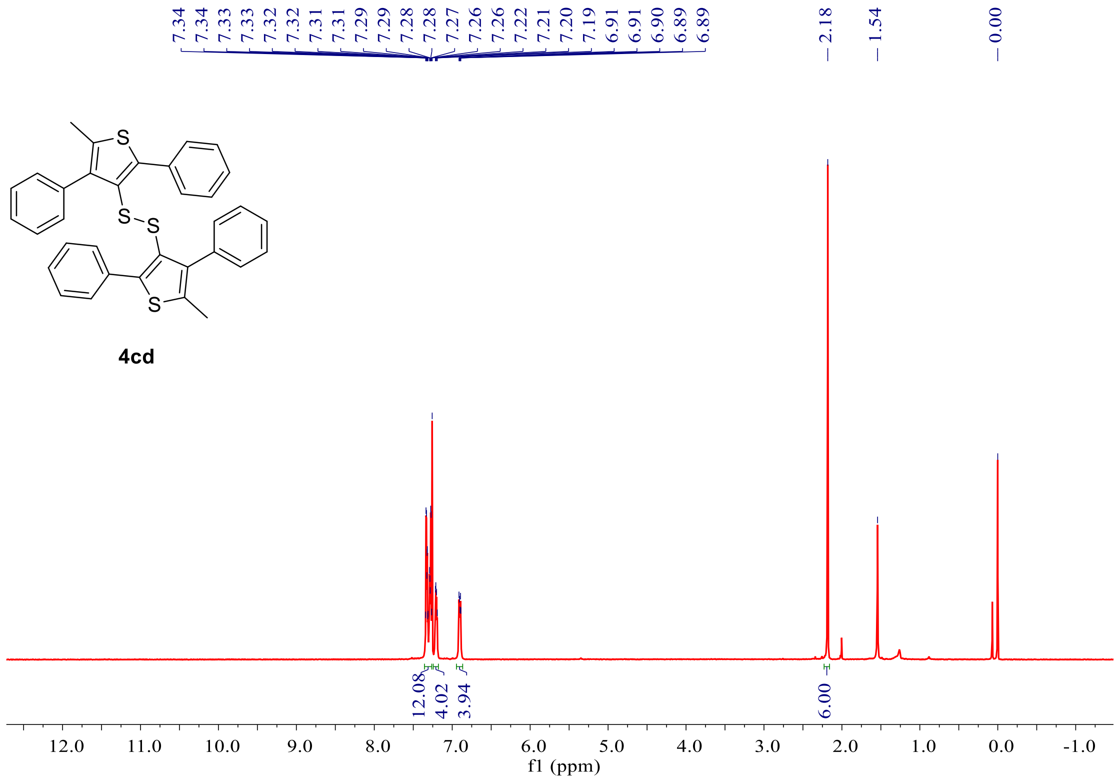
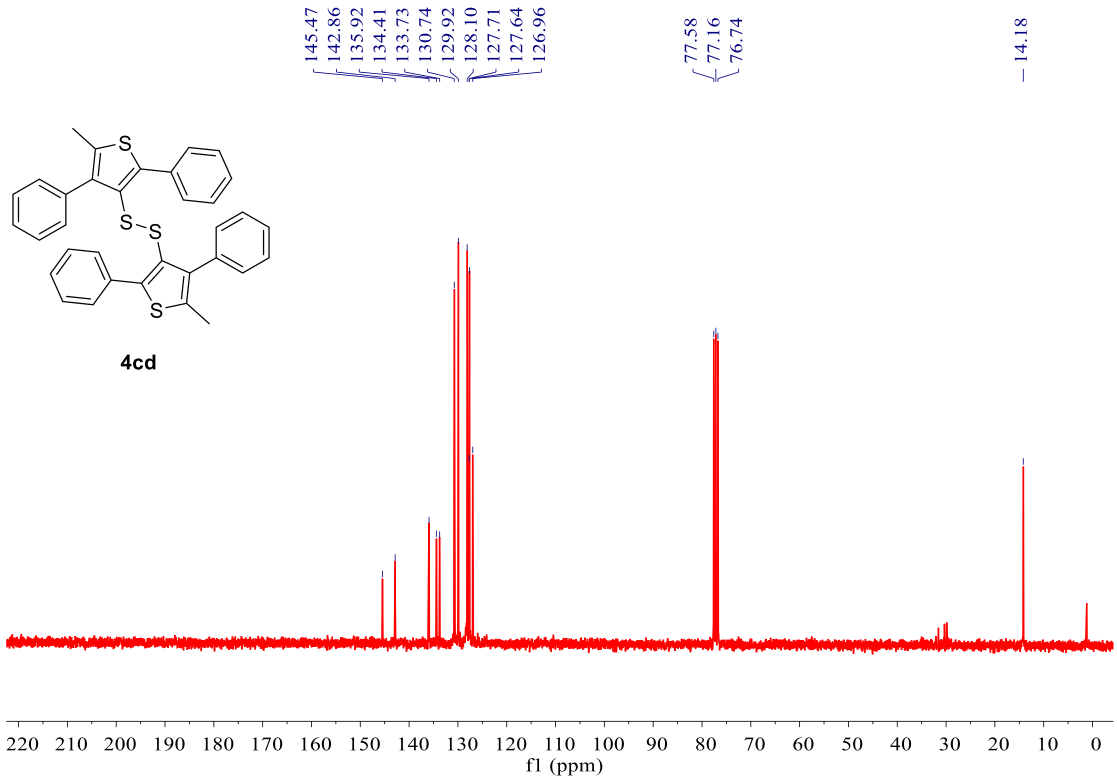
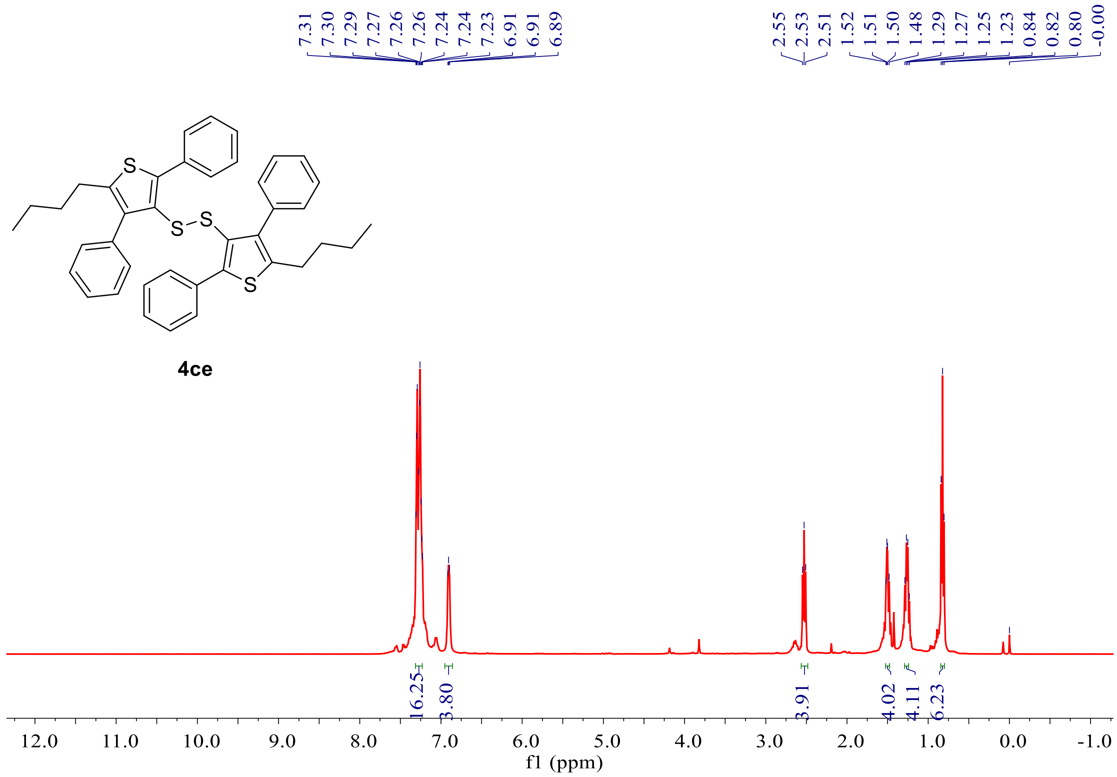
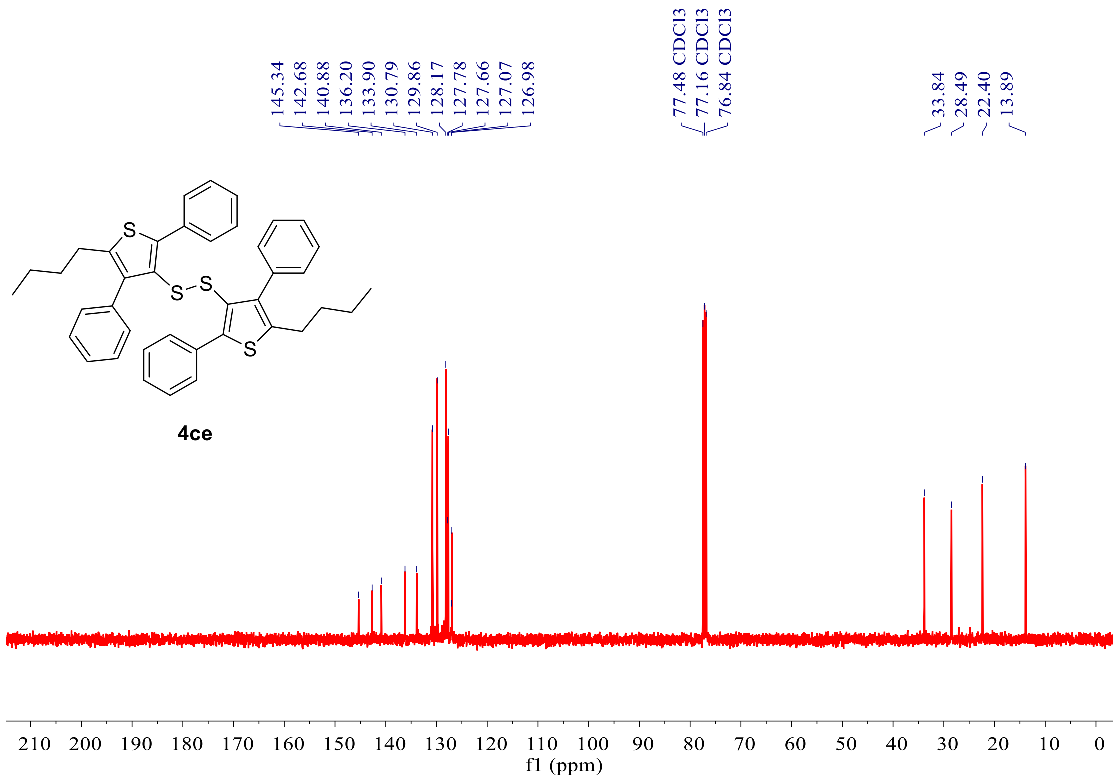
f1 (ppm)

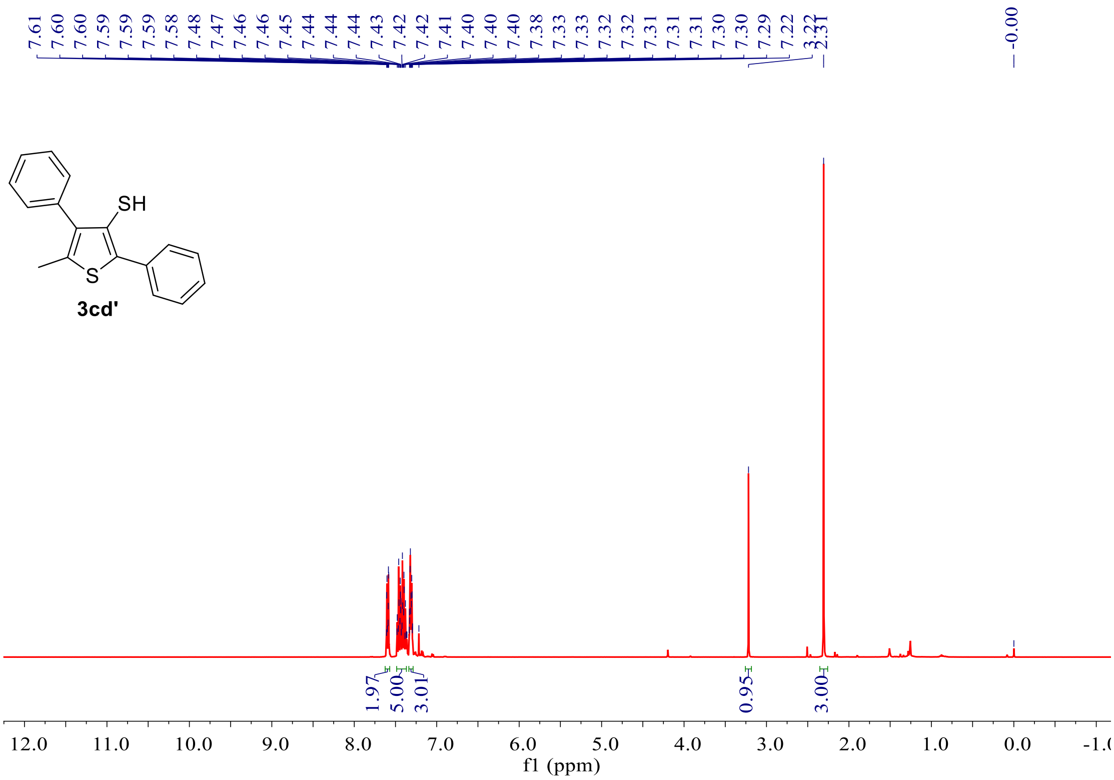

149.99
149.04
143.58
142.27
140.05
136.77
135.48
133.26
130.99
129.46
129.04
128.52
128.02
127.88
127.43
123.01
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
4ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

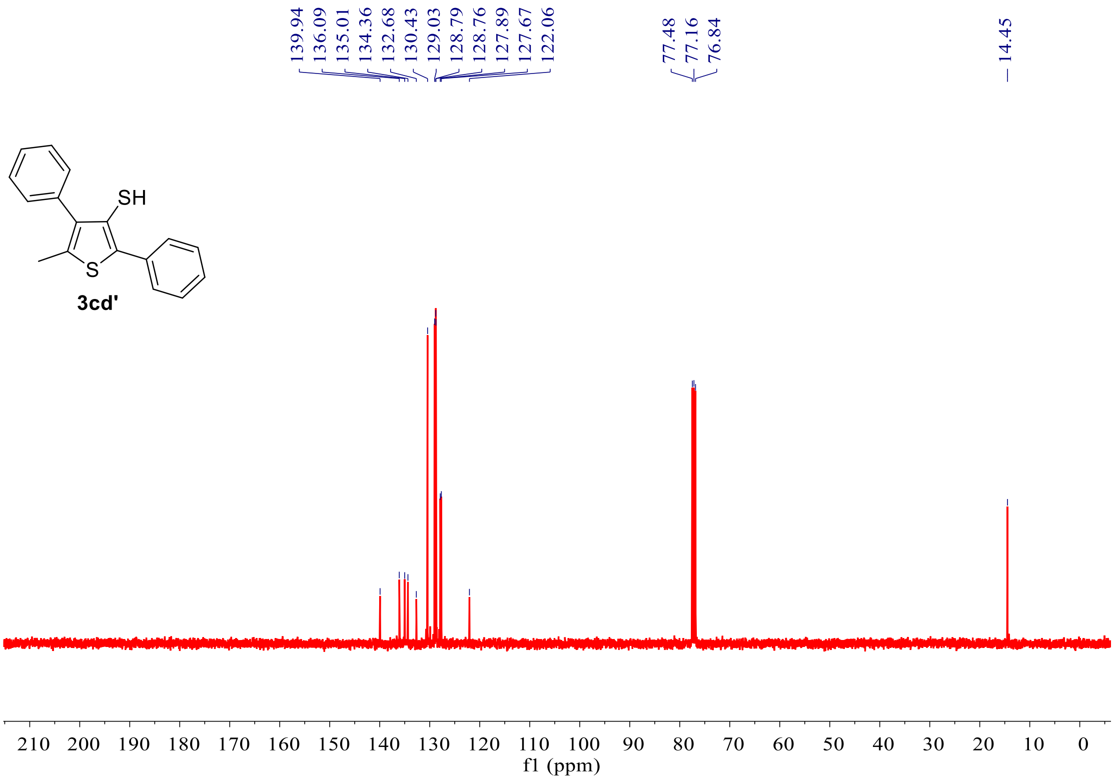

7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.22
7.21
7.20
7.19
6.91
6.91
6.90
6.89
6.89
2.18
1.54
0.00
4cd
12.08
4.02
3.94
6.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


145.47
142.86
135.92
134.41
133.73
130.74
129.92
128.10
127.71
127.64
126.96
77.58
77.16
76.74
14.18
4cd
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

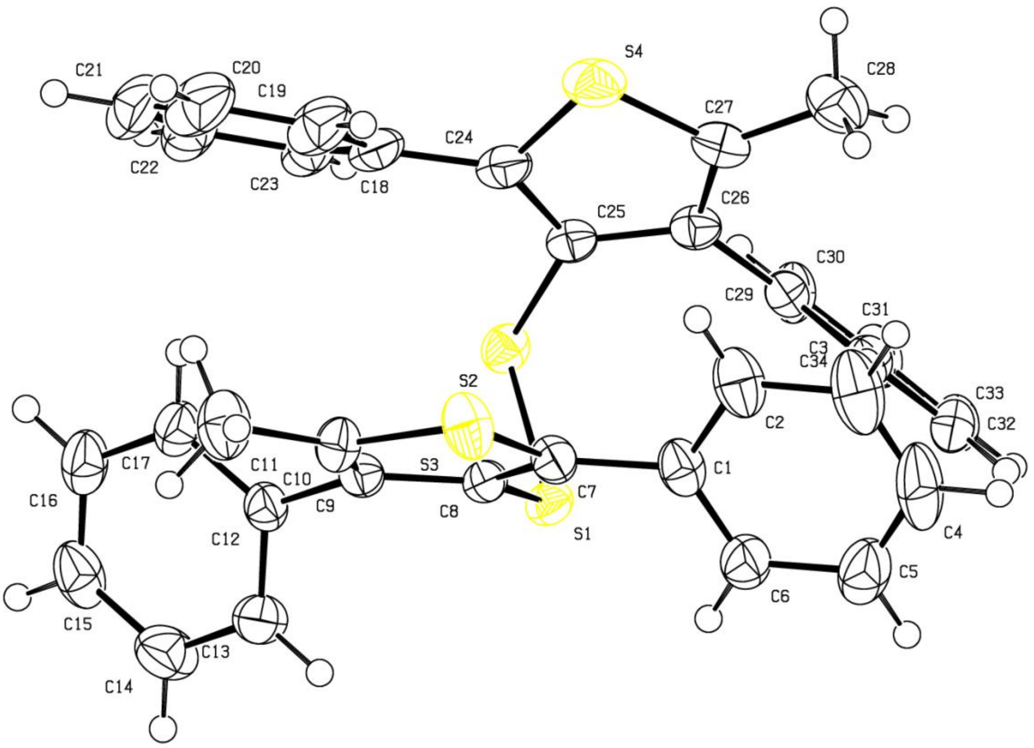

7.31 7.30 7.29 7.27 7.26 7.26 7.24 7.24 7.23 6.91 6.91 6.89
2.55 2.53 2.51 1.52 1.51 1.50 1.48 1.29 1.27 1.25 1.23 0.84 0.82 0.80 -0.00
4ce
16.25 3.80 3.91 4.02 4.11 6.23
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


145.34 142.68 140.88 136.20 133.90 130.79 129.86 128.17 127.78 127.66 127.07 126.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
33.84 28.49 22.40 13.89
4ce
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.61 7.60 7.60 7.59 7.59 7.59 7.58 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.42 7.42 7.41 7.40 7.40 7.40 7.38 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.22 3.22 2.31
-0.00
SH
S
3cd'
1.97
5.00
3.01
0.95
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


139.94 136.09 135.01 134.36 132.68 130.43 129.03 128.79 128.76 127.89 127.67 122.06
77.48 77.16 76.84
14.45
SH
S
3cd'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

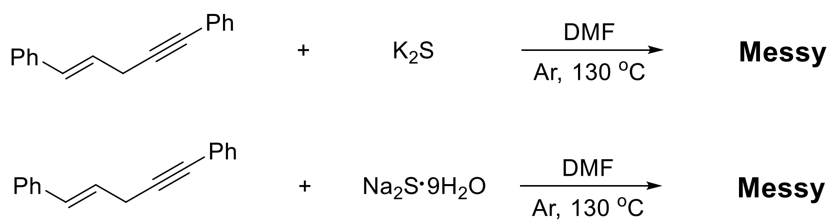
10. X-ray Structure of 4aa



CCDC 1901393 (**4aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

11. The reaction of 1,4-enynes

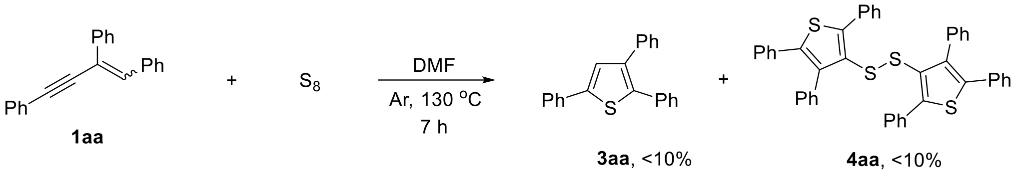
The following two reactions have been done to test the reactivity of 1,4-enynes. The results show that 1,4-enynes are not suitable for the sulfur insertion reaction under the optimized conditions.



12. The reaction of 1aa under other conditions

We have tried the reactions of **1aa** in the presence of S_8. It was found that **3aa** and **4aa** were both observed in <10% yields, respectively.

S_8 alone:



We have also tried the reactions of **1aa** under Prof. Li's conditions (Y. Liu, J.-L. Zhang, R.-J. Song and J.-H. Li, *Org. Lett.* 2014, **16**, 5838–5841). The reaction of K_2S with **1aa** catalysed by $CuCl_2$ afforded **3aa** and **4aa** in 18% and 43% yields, respectively. The reaction of $Na_2S{\cdot}9H_2O$ with **1aa** catalysed by $CuCl_2$ furnished **3aa** in 82% yield and **4aa** was not observed. The reaction of KSCN with **1aa** under Prof. Li's another reaction conditions (J.-X. Yu, S. Niu, M. Hu, J.-N. Xiang and J.-H. Li, *Chem. Commun.* 2019, DOI: 10.1039/c9cc02242b.) failed to give the desired products.

Li's condition: