

Supplementary Information

**Synthesis Of 1,4-Dithiins And 1,4-Diselenins From Alkynes And
Elemental Sulfur/Selenium Under Transition-Metal-Free Conditions
With High Regioselectivity**

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Table of contents

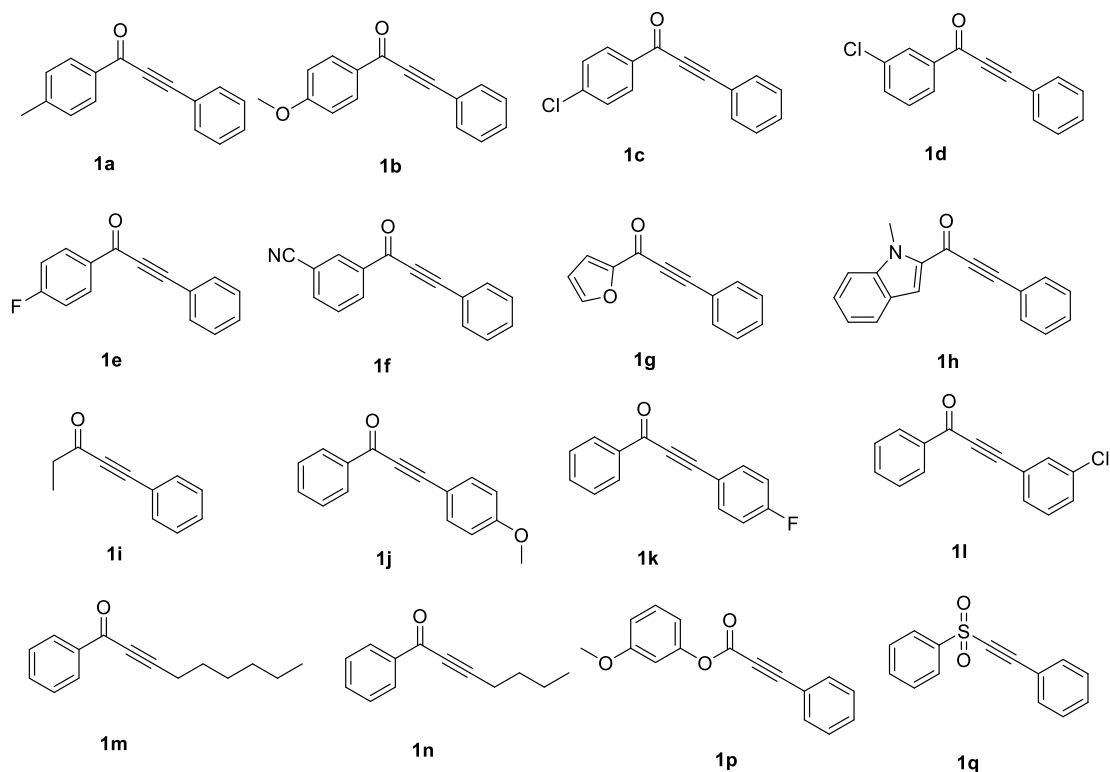
1. General information	- 2 -
2. Synthesis of alkynones 1	- 3 -
3. Experimental Section.....	- 4 -
3.1 General procedure for the synthesis of 1,4-dithiins 3 and 3'	- 4 -
3.2 General procedure for the synthesis of 1,4-diselenin 4 and 4'	- 5 -
3.3 Characterization data of products	- 6 -
3.4 Further transformations of 3a	- 17 -
3.5 Gram-scale experiment.....	- 20 -
4. References	- 21 -
5. Copies of NMR spectra	- 22 -
6. X-Ray Crystal Structure of 3h (CCDC: 2201657)	- 50 -

1. General information

Unless otherwise stated, all experiments were carried out under the atmosphere of nitrogen gas. Visualization of spots on TLC plate was accomplished with UV light (254 nm). All commercial reagents were used without further purification. Reactions were monitored by thin layer chromatography. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). NMR spectra were recorded on Bruker AV-500 or Bruker AV-600 NMR spectrometer. ¹H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) as internal reference; ¹³C NMR spectra was recorded with CDCl₃ ($\delta = 77.00$ ppm) as internal reference. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, m = multiplet. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FTICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractometers.

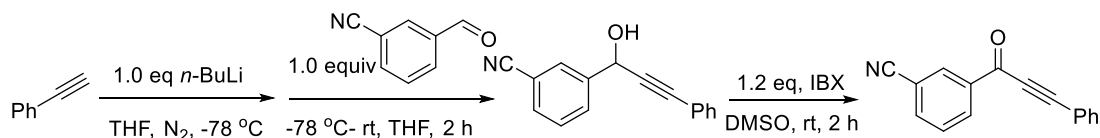
2. Synthesis of alkynones 1

All the substrates **1** are known compounds and have been prepared according to methods reported in the previous literature.



1a, **1b**, **1c**, **1e**, **1j**, **1k**¹; **1h**²; **1d**, **1g**³, **1i**⁴, **1l**⁵, **1m**⁶, **1n**⁷, **1p**⁸, **1q**⁹

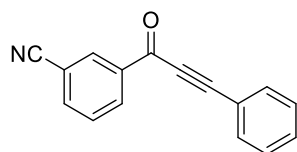
Synthesis of **1f**



To a solution of alkyne (12 mmol) in anhydrous THF (30 mL), *n*-BuLi (2.5M, 10 mmol, 4 mL) was added at -78 °C. The resulting mixture was stirred at -78 °C for 1 h, then the aldehyde (10 mmol) was added and the reaction temperature was raised to room temperature till aldehyde disappeared by TLC analysis. The resulting mixture was quenched with a saturated solution of NH₄Cl and extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 5:1 as the eluent afforded the

substituted alkynol.

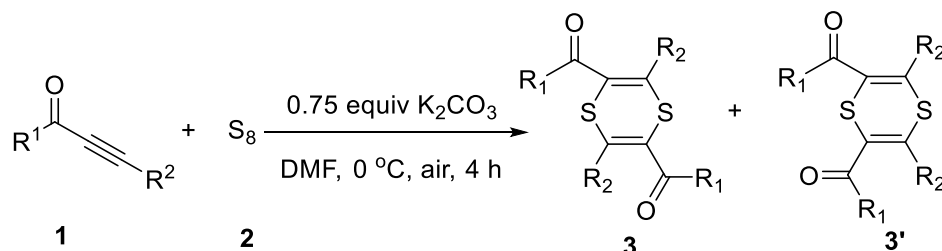
To a solution of substituted alkynol (10 mmol) in DMSO (20 mL) in round-bottom flask, IBX (12 mmol, 3.36 g) was added at room temperature. The reaction was stirred in air until the full conversion of substituted alkynol monitored by thin-layer chromatography. The resulting mixture was quenched with water (20 mL) and filtered. Then the filtrate was extracted with ethyl acetate (20 mL \times 3). The organic layers was combined, washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/ethyl acetate = 10:1 as white solid in 65% yield.



¹H NMR (500 MHz, CDCl₃) δ 8.50 (s, 1H), 8.44-8.42 (m, 1H), 7.92-7.90 (m, 1H), 7.73-7.66 (m, 3H), 7.56-7.51 (m, 1H), 7.48-7.44 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 175.59, 137.53, 136.77, 133.25, 133.19, 133.10, 131.36, 129.69, 128.81, 119.36, 117.78, 113.23, 95.02, 86.12. m.p. 126 - 128 °C. HRMS (ESI) calcd for C₁₆H₁₀NO [M + H]⁺: 232.0757, found: 232.0761.

3. Experimental Section

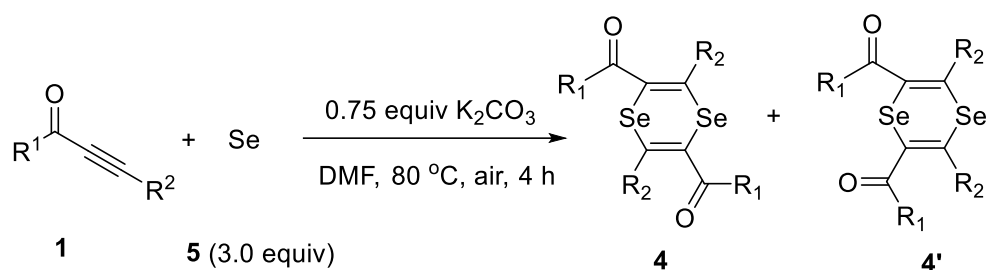
3.1 General procedure for the synthesis of 1,4-dithiins **3** and **3'**



In an oven-dried Schlenk tube was charged with a stir bar, alkynones **1** (0.30 mmol, 1.0 equiv), elemental sulfur **2** (0.05 mmol, 12.8 mg), K₂CO₃ (0.225 mmol, 31.1 mg) and

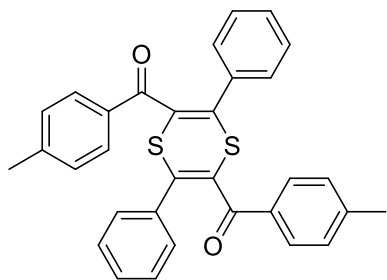
DMF (3.0 mL). The mixture was stirred at 0 °C for 4 hours. Upon completion of the reaction, the reaction mixture was quenched by water. The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The products **3** and **3'** were isolated by column chromatography on silica gel (eluted with PE/EA, v:v) and the ratio of **3** and **3'** was analyzed by calculating peak areas in ¹H NMR spectra.

3.2 General procedure for the synthesis of 1,4-diselenin **4** and **4'**

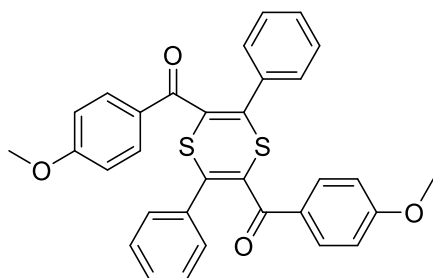


In an oven-dried Schlenk tube was charged with a stir bar, alkynones **1** (0.30 mmol, 1.0 equiv), elemental selenium **5** (0.90 mmol, 71.1 mg), K₂CO₃ (0.225 mmol, 31.1 mg) and DMF (3.0 mL). The mixture was stirred at 80 °C for 4 hours. Upon completion of the reaction, the reaction mixture was quenched by water. The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The products **4** and **4'** were isolated by column chromatography on silica gel (eluted with PE/EA, v:v) and the ratio of **4** and **4'** was analyzed by calculating the ratio of peak areas in ¹H NMR spectra.

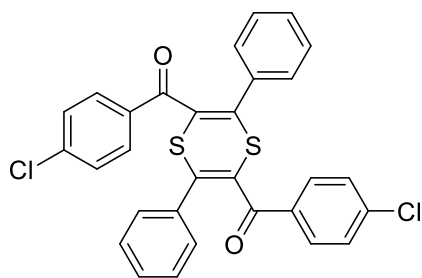
3.3 Characterization data of products



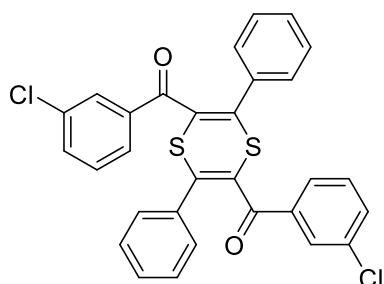
(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis(p-tolylmethanone) (3a) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 10:1, v/v) to provide the desired compound as a yellow solid (**3a:3a'** = 7:1, 71.2 mg, 94% total yield). m.p. 156 - 158 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.76 - 7.73 (m, 4H), 7.37 - 7.33 (m, 4H), 7.19 - 7.10 (m, 10H), 2.36 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 191.48, 146.56, 144.98, 135.08, 132.56, 130.94, 129.70, 129.64, 129.55, 129.44, 128.40, 21.75. HRMS (ESI) calcd for C₃₂H₂₄O₂S₂Na [M + Na]⁺: 527.1110, found: 527.1108.



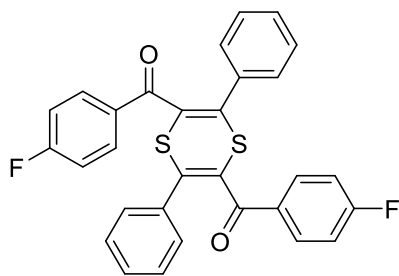
(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis((4-methoxyphenyl)methanone) (3b) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 10:1, v/v) to provide the desired compound as a yellow solid (**3b:3b'** = 5:1, 72.4 mg, 90% total yield). m.p. 189 - 191 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.84 - 7.82 (m, 4H), 7.38 - 7.35 (m, 4H), 7.17 - 7.13 (m, 6H), 6.86 - 6.84 (m, 4H), 3.83 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 190.50, 164.18, 146.10, 135.19, 132.03, 131.19, 129.59, 129.51, 128.41, 128.02, 114.02, 55.51. HRMS (ESI) calcd for C₃₂H₂₄O₄S₂Na [M + Na]⁺: 559.1008, found: 529.1003.



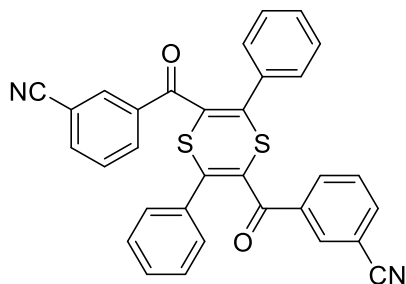
(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis((4-chlorophenyl)methanone) (3c) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 12:1, v/v) to provide the desired compound as a yellow solid (**3c:3c'** = 11:1, 73.5 mg, 90% total yield). m.p. 128 - 130 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.76 - 7.72 (m, 4H), 7.35 - 7.29 (m, 8H), 7.23 - 7.13 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 190.43, 148.11, 140.44, 134.80, 133.53, 130.78, 130.12, 130.05, 129.64, 129.10, 128.64. HRMS (ESI) calcd for C₃₀H₁₈Cl₂O₂S₂Na [M + Na]⁺: 567.0018, found: 567.0013.



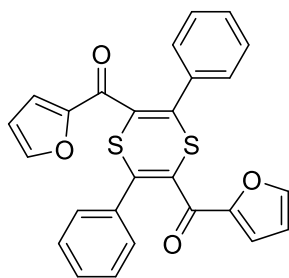
(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis((3-chlorophenyl)methanone) (3d) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 12:1, v/v) to provide the desired compound as a yellow solid (**3d:3d'** = 7:1, 70.0 mg, 82% total yield). m.p. 138 - 140 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.78 - 7.77 (m, 2H), 7.66 - 7.63 (m, 2H), 7.45 - 7.42 (m, 2H), 7.34 - 7.27 (m, 6H), 7.22 - 7.14 (m, 6H) ¹³C NMR (125 MHz, CDCl₃) δ 190.28, 148.72, 136.73, 134.94, 134.79, 133.64, 130.12, 130.02, 129.77, 129.64, 129.34, 128.62, 127.46. HRMS (ESI) calcd for C₃₀H₁₈Cl₂O₂S₂Na [M + Na]⁺: 567.0018, found: 567.0012.



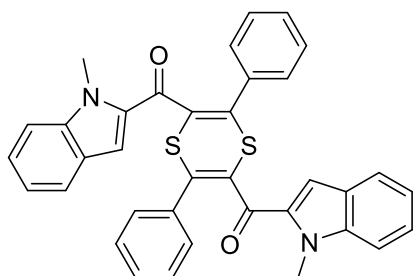
(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis((4-fluorophenyl)methanone) (3e) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 12:1, v/v) to provide the desired compound as a yellow solid (**3d:3d'** = 12:1, 70.7 mg, 92% total yield). m.p. 136 - 138 °C. ^{13}C NMR (125 MHz, CDCl_3) δ 7.85 - 7.82 (m, 4H), 7.34 - 7.31 (m, 4H), 7.22 - 7.13 (m, 6H), 7.06 - 7.01 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 190.14, 166.05 (d, $J = 255.0$ Hz), 147.80, 134.88, 132.16 (d, $J = 10.0$ Hz), 131.56 (d, $J = 2.50$ Hz), 130.35, 129.94, 129.61, 128.57, 115.99 (d, $J = 21.25$ Hz). **HRMS** (ESI) calcd for $\text{C}_{30}\text{H}_{18}\text{F}_2\text{O}_2\text{S}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 535.0609, found: 535.0601.



3,3'-(3,6-diphenyl-1,4-dithiine-2,5-dicarbonyl)dibenzonitrile (3f) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 8:1, v/v) to provide the desired compound as a red solid (**3f:3f'** = 3:1, 67.9 mg, 86% total yield). m.p. 146 - 148 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.03 - 8.01 (m, 2H), 7.95 - 7.91 (m, 2H), 7.73 - 7.70 (m, 2H), 7.52 - 7.48 (m, 2H), 7.32 - 7.29 (m, 4H), 7.23 - 7.15 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 189.29, 150.32, 136.32, 136.16, 134.57, 132.93, 132.84, 130.57, 129.78, 129.76, 128.82, 128.75, 117.51, 113.22. **HRMS** (ESI) calcd for $\text{C}_{32}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 549.0702, found: 549.0696.

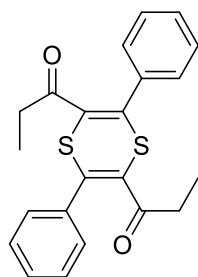


(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis(furan-2-ylmethanone) (3g) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 11:1, v/v) to provide the desired compound as a yellow solid (**3g**:**3g'** = 12:1, 65.1 mg, 95% total yield). m.p. 167 - 169 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.47 - 7.40 (m, 6H), 7.27 - 7.18 (m, 6H), 7.04 - 7.01 (m, 2H), 6.40 - 6.37 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 178.89, 150.96, 149.96, 147.68, 135.12, 129.87, 129.68, 128.83, 128.52, 120.56, 112.61. HRMS (ESI) calcd for C₂₆H₁₆O₄S₂Na [M + Na]⁺: 479.0382, found: 479.0374.

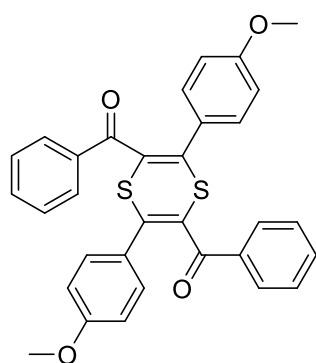


(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis((1-methyl-1H-indol-2-yl)methanone) (3h) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 7:1, v/v) to provide the desired compound as a yellow solid (**3h**:**3h'** = 9:1, 77.8 mg, 89% total yield). ¹H NMR (500 MHz, CDCl₃) δ 7.64-7.61 (m, 2H), 7.48-7.45 (m, 4H), 7.40-7.34 (m, 4H), 7.19 (s, 2H), 7.16-7.11 (m, 8H), 4.08 (s, 6H). m.p. 178 - 180 °C. ¹³C NMR (125 MHz, CDCl₃) δ 184.08, 147.05, 140.95, 135.49, 133.85, 131.41, 129.56, 129.53, 128.46, 126.71, 125.86, 123.36, 120.99, 115.10, 110.40, 31.98. HRMS (ESI) calcd for C₃₆H₂₆N₂O₂S₂Na [M + Na]⁺: 605.1328, found: 605.1321. **3h'**: ¹H NMR (500 MHz, CDCl₃) δ 7.64-7.60 (m, 6H), 7.34-7.24 (m, 10H), 7.21 (s, 2H), 7.11-7.07 (m, 2H), 3.92 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 183.00, 146.80, 140.75, 135.71, 133.70, 130.42, 129.61, 129.45, 128.63, 126.53, 125.78, 123.31,

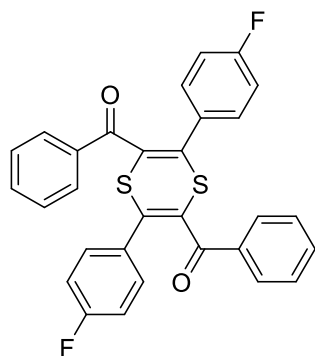
120.83, 114.91, 110.27, 31.81. m.p. 176 - 178 °C. **HRMS** (ESI) calcd for C₃₆H₂₇N₂O₂S₂ [M + H]⁺: 583.1509, found: 583.1509.



1,1'-(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis(propan-1-one) (3i) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 15:1, v/v) to provide the desired compound as a yellow solid (**3i:3i'** = 10:1, 35.4 mg, 62% total yield). m.p. 143 - 145 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.43 - 7.38 (m, 10H), 2.29 - 2.24 (m, 4H), 0.98 - 0.94 (m, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 200.28, 149.06, 135.64, 131.15, 130.22, 129.58, 128.81, 35.70, 8.51. **HRMS** (ESI) calcd for C₂₂H₂₀O₂S₂Na [M + Na]⁺: 403.0797, found: 403.0788.

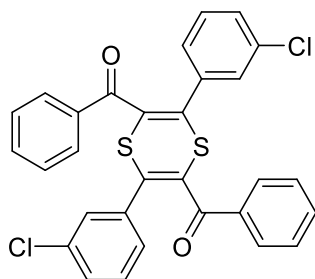


(3,6-bis(4-methoxyphenyl)-1,4-dithiine-2,5-diyl)bis(phenylmethanone) (3j) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 10:1, v/v) to provide the desired compound as a yellow solid (**3j:3j'** = 12:1, 74.1 mg, 92% total yield). m.p. 168 - 170 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.84 - 7.81 (m, 4H), 7.52 - 7.49 (m, 2H), 7.38 - 7.34 (m, 4H), 7.30 - 7.26 (m, 4H), 3.67 (s, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 192.16, 160.73, 149.07, 135.34, 133.65, 131.32, 129.49, 128.61, 128.26, 127.38, 113.82, 55.19. **HRMS** (ESI) calcd for C₃₂H₂₄O₄S₂Na [M + Na]⁺: 559.1008, found: 559.0999.



(3,6-bis(4-fluorophenyl)-1,4-dithiine-2,5-diyl)bis(phenylmethanone) (3k)

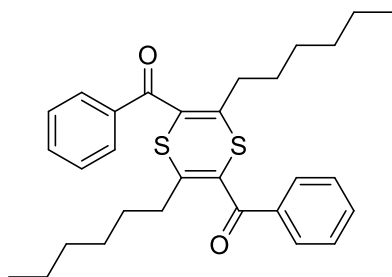
Following the general procedure, the crude product was purified by column chromatography (PE/EA = 10:1, v/v) to provide the desired compound as a yellow solid (**3k:3k'** = 6:1, 66.9 mg, 87% total yield). m.p. 180 - 182 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.83 - 7.80 (m, 4H), 7.56 - 7.51 (m, 2H), 7.41 - 7.37 (m, 4H), 7.34 - 7.30 (m, 4H), 6.84 - 6.80 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 191.58, 163.4 (d, *J* = 250.0 Hz) 146.70, 135.07, 134.07, 131.71 (d, *J* = 8.75 Hz), 131.00 (d, *J* = 3.75 Hz), 130.57, 129.47, 128.82, 115.67 (d, *J* = 22.5 Hz). HRMS (ESI) calcd for C₃₀H₁₈F₂O₂S₂Na [M + Na]⁺: 535.0609, found: 535.0603.



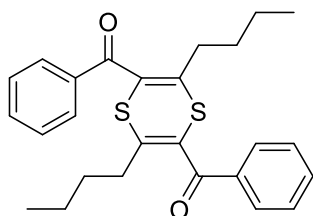
(3,6-bis(3-chlorophenyl)-1,4-dithiine-2,5-diyl)bis(phenylmethanone) (3l)

Following the general procedure, the crude product was purified by column chromatography (PE/EA = 13:1, v/v) to provide the desired compound as a yellow solid (**3l:3l'** = 6:1, 76.9 mg, 94% total yield). m.p. 124 - 126 °C. ¹H NMR (600 MHz, CDCl₃) 7.83-7.80 (m, 4H), 7.57-7.53 (m, 2H), 7.43-7.40 (m, 4H), 7.33-7.31 (m, 2H), 7.22-7.19 (m, 2H), 7.16-7.13 (m, 2H), 7.08-7.05 (m 2H). ¹³C NMR (150 MHz, CDCl₃) δ 191.18, 145.49, 136.53, 135.03, 134.45, 134.17, 131.96, 129.86, 129.70, 129.49, 129.42,

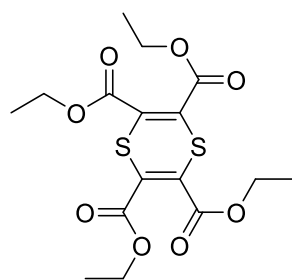
128.86, 127.93. **HRMS** (ESI) calcd for $C_{30}H_{18}Cl_2O_2S_2Na$ $[M + Na]^+$: 567.0018, found: 567.0017.



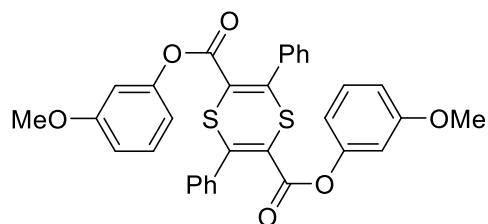
(3,6-dihexyl-1,4-dithiine-2,5-diyl)bis(phenylmethanone) (3m) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 20:1, v/v) to provide the desired compound as a yellow oil (55.4 mg, 75%). **1H NMR** (500 MHz, $CDCl_3$) δ 7.89 - 7.86 (m, 4H), 7.65 - 7.61 (m, 2H), 7.53 - 7.49 (m, 4H), 2.43 - 2.39 (m, 4H), 1.52 - 1.48 (m, 4H), 1.20 - 1.11 (m, 12H), 0.81 - 0.77 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.57, 147.80, 135.97, 133.93, 130.71, 129.52, 128.72, 34.99, 31.26, 28.91, 28.63, 22.35, 13.92. **HRMS** (ESI) calcd for $C_{30}H_{36}O_2S_2Na$ $[M + Na]^+$: 515.2049, found: 515.2045.



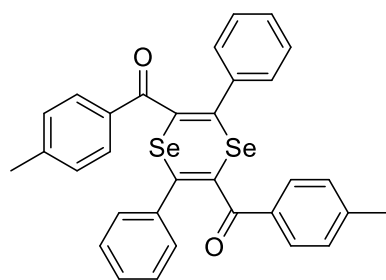
(3,6-dibutyl-1,4-dithiine-2,5-diyl)bis(phenylmethanone) (3n) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 20:1, v/v) to provide the desired compound as a yellow oil (43.9 mg, 67%). **1H NMR** (500 MHz, $CDCl_3$) δ 7.88 - 7.85 (m, 4H), 7.65 - 7.61 (m, 2H), 7.53 - 7.48 (m, 4H), 2.55 - 2.51 (m, 4H), 1.53 - 1.46 (m, 4H), 1.24 - 1.18 (m, 4H), 0.79 - 0.75 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.06, 147.99, 135.91, 133.97, 131.39, 129.38, 128.78, 36.75, 31.93, 22.11, 13.64. **HRMS** (ESI) calcd for $C_{26}H_{28}O_2S_2Na$ $[M + Na]^+$: 459.1423, found: 459.1418.



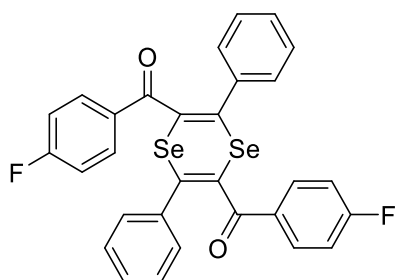
tetraethyl 1,4-dithiine-2,3,5,6-tetracarboxylate (3o) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 25:1, v/v) to provide the desired compound as a yellow solid (24.9 mg, 41%). m.p. 114 - 116 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.86 - 7.82 (m, 4H), 7.35 - 7.32 (m, 4H), 7.21 - 7.13 (m, 6H), 7.05 - 7.01 (m, 4H). **¹³C NMR** (125 MHz, CDCl₃) δ 190.08, 167.01, 164.97, 147.78, 134.82, 132.16, 132.08, 131.50, 131.48, 130.27, 129.90, 129.56, 128.53, 116.04, 115.86. **HRMS** (ESI) calcd for C₁₆H₂₀O₈S₂Na [M + Na]⁺: 427.0492, found: 427.0485.



bis(3-methoxyphenyl) 3,6-diphenyl-1,4-dithiine-2,5-dicarboxylate (3p) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 10:1, v/v) to provide the desired compound as a yellow solid (**3p:3p'** = 6:1, 64.2 mg, 75% total yield). m.p. 128 - 130 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.59-7.56 (m, 4H), 7.45-7.41 (m, 6H), 7.26-7.18 (m, 2H), 6.75-6.72 (m, 2H), 6.54-6.51 (m, 2H), 6.41-6.39 (m, 2H), 3.74 (s, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 161.29, 160.33, 155.25, 151.15, 135.82, 130.18, 129.71, 129.53, 128.58, 120.42, 113.15, 111.97, 106.89, 55.42. **HRMS** (ESI) calcd for C₃₂H₂₄O₆S₂Na [M + Na]⁺: 591.0907, found: 591.0913.

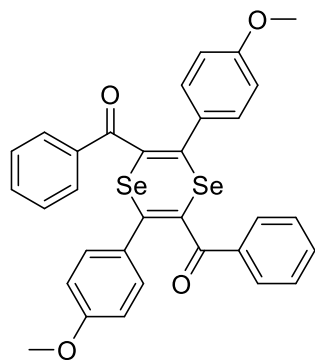


(3,6-diphenyl-1,4-diselenine-2,5-diyl)bis(p-tolylmethanone) (4a) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 9:1, v/v) to provide the desired compound as a yellow solid (**4a:4a'** = 10:1, 82.6 mg, 92% total yield). m.p. 158 - 160 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.73 - 7.71 (m, 4H), 7.37 - 7.34 (m, 4H), 7.17 - 7.10 (m, 10H), 2.36 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 193.09, 147.02, 144.81, 136.92, 132.43, 131.90, 129.85, 129.61, 129.38, 129.24, 128.32, 21.74. HRMS (ESI) calcd for C₃₂H₂₄O₂Se₂Na [M + Na]⁺: 622.9999, found: 622.9994.



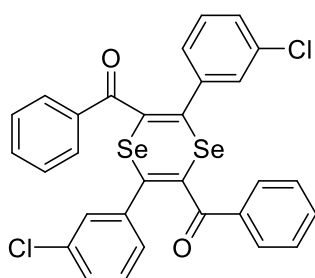
(3,6-diphenyl-1,4-diselenine-2,5-diyl)bis((4-fluorophenyl)methanone) (4b)

Following the general procedure, the crude product was purified by column chromatography (PE/EA = 12:1, v/v) to provide the desired compound as a yellow solid (**4b:4b'** = 7:1, 74.6 mg, 82% total yield). m.p. 136 - 138 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.83 - 7.79 (m, 4H), 7.35 - 7.32 (m, 4H), 7.20 - 7.11 (m, 6H), 7.04 - 6.99 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 191.78, 165.99 (d, *J* = 255.0 Hz), 148.27, 136.72, 132.05 (d, *J* = 8.75 Hz), 131.38 (d, *J* = 3.75 Hz), 131.26, 129.79, 129.63, 128.51, 115.92 (d, *J* = 22.5 Hz). HRMS (ESI) calcd for C₃₀H₁₈F₂O₂Se₂Na [M + Na]⁺: 630.9498, found: 630.9492.



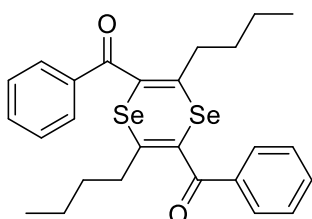
(3,6-bis(4-methoxyphenyl)-1,4-diselenine-2,5-diyl)bis(phenylmethanone) (4c)

Following the general procedure, the crude product was purified by column chromatography (PE/EA = 8:1, v/v) to provide the desired compound as a yellow solid (**4c:4c'** = 9:1, 73.8 mg, 78% total yield). m.p. 170 - 172 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.82-7.79 (m, 4H), 7.49-7.46 (m, 2H), 7.37-7.33 (m, 4H), 7.30-7.27 (m, 4H), 6.63-6.60 (m, 4H), 3.66 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 193.78, 160.40, 149.11, 135.06, 133.57, 131.46, 129.52, 129.40, 129.27, 128.56, 113.73, 55.18. HRMS (ESI) calcd for C₃₂H₂₄O₄Se₂Na [M + Na]⁺: 654.9897, found: 654.9891.



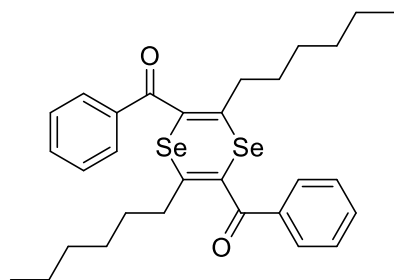
(3,6-bis(3-chlorophenyl)-1,4-diselenine-2,5-diyl)bis(phenylmethanone) (4d)

Following the general procedure, the crude product was purified by column chromatography (PE/EA = 8:1, v/v) to provide the desired compound as a yellow solid (**4d:4d'** = 3:1, 72.9 mg, 76% total yield). m.p. 156 - 158 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.81 - 7.78 (m, 4H), 7.55 - 7.51 (m, 2H), 7.42 - 7.38 (m, 4H), 7.34 - 7.32 (m, 2H), 7.23 - 7.20 (m, 2H), 7.06 - 7.02 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 192.72, 145.93, 138.27, 134.78, 134.25, 134.03, 132.87, 129.60, 129.59, 129.49, 129.24, 128.76, 127.99. HRMS (ESI) calcd for C₃₀H₁₈Cl₂O₂Se₂Na [M + Na]⁺: 662.8907, found: 662.8899.



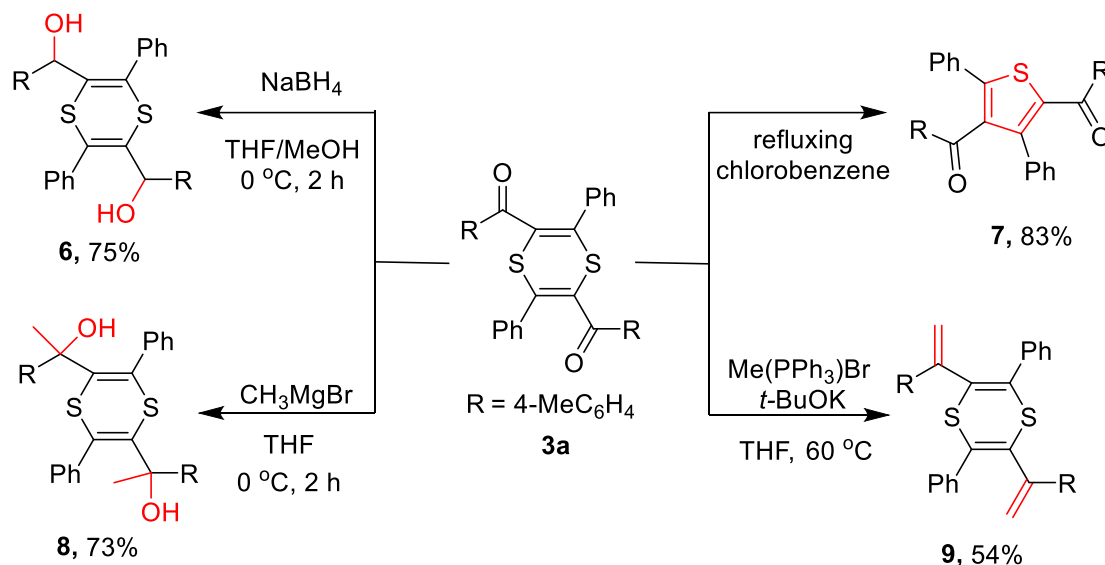
(3,6-dibutyl-1,4-diselenine-2,5-diyl)bis(phenylmethanone) (4f) Following the general procedure, the crude product was purified by column chromatography (PE/EA

= 15:1, v/v) to provide the desired compound as a yellow oil (39.0 mg, 49%). **¹H NMR** (500 MHz, CDCl₃) δ 7.88 - 7.85 (m, 4H), 7.65 - 7.61 (m, 2H), 7.53 - 7.48 (m, 4H), 2.55 - 2.51 (m, 4H), 1.53 - 1.46 (m, 4H), 1.24 - 1.18 (m, 4H), 0.79 - 0.75 (m, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 193.06, 147.99, 135.91, 133.97, 131.39, 129.38, 128.78, 36.75, 31.93, 22.11, 13.64. **HRMS** (ESI) calcd for C₂₆H₂₈O₂Se₂Na [M + Na]⁺: 555.0312, found: 555.0317.

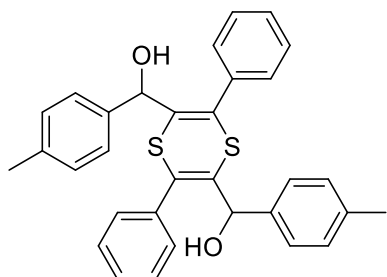


(3,6-dihexyl-1,4-diselenine-2,5-diyl)bis(phenylmethanone) (4g) Following the general procedure, the crude product was purified by column chromatography (PE/EA = 15:1, v/v) to provide the desired compound as a yellow oil (59.8 mg, 68%). **¹H NMR** (500 MHz, CDCl₃) δ 7.89 - 7.86 (m, 4H), 7.63 - 7.61 (m, 2H), 7.52 - 7.48 (m, 4H), 2.55 - 2.51 (m, 4H), 1.52 - 1.48 (m, 4H), 1.20 - 1.10 (m, 12H), 0.81 - 0.77 (m, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 193.01, 148.00, 135.91, 133.94, 131.37, 129.37, 128.75, 36.97, 31.25, 29.77, 28.59, 22.33, 13.92. **HRMS** (ESI) calcd for C₃₀H₃₆O₂Se₂Na [M + Na]⁺: 611.0938, found: 611.0936.

3.4 Further transformations of 3a



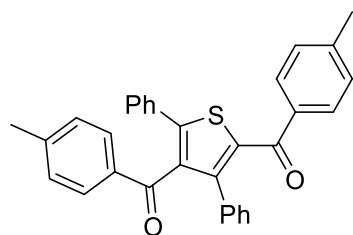
Procedure for preparation of **6**¹⁰: To an oven-dried 10 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, **3a** (0.2 mmol, 1.0 equiv., 100.9 mg) are diluted in dry THF and methanol (THF: MeOH=1:1, v: v) at 0 °C. NaBH₄ (0.6 mmol, 3.0 equiv., 22.7 mg) was added to the reaction vessel, and the reaction was stirred for 2 h at 0 °C under N₂ atmosphere. Upon the completion of reaction monitored by TLC, and the reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure, the pure product was isolated by column chromatography on silica gel (PE: EA = 7: 1, v: v) as white solid. (76.0 mg, 75%)



¹H NMR (500 MHz, CDCl₃) δ 7.27 - 7.25 (m, 10H), 7.17 - 7.10 (m, 8H), 5.66 - 5.63 (m, 2H), 2.50 - 2.48 (m, 2H), 2.35 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 140.09,

138.80, 138.52, 137.46, 136.82, 129.33, 129.08, 128.58, 128.43, 125.95, 72.39, 21.07. m.p. 105 - 107 °C. **HRMS** (ESI) calcd for C₃₂H₂₈O₂S₂Na [M + Na]⁺: 531.1423, found: 531.1428.

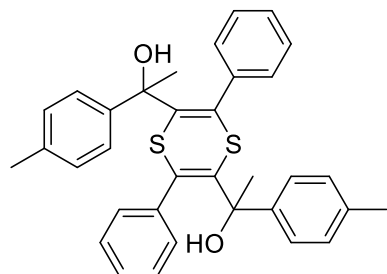
Procedure for preparation of **7**¹¹: To a 10 mL sealed tube charged with a PTFE-coated magnetic stirring bar and **3a** (0.2 mmol, 1.0 equiv., 100.9 mg) The reaction was carried out in refluxing chlorobenzene (2 mL) for 1 h. Upon the completion of reaction monitored by TLC, and the reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure, the pure product was isolated by column chromatography on silica gel (PE: EA = 6: 1, v: v) as yellow solid. (78.5 mg, 83%)



¹H NMR (500 MHz, CDCl₃) δ 7.57-7.47 (m, 6H), 7.30-7.25 (m, 3H), 7.10-7.07 (m, 2H), 7.01-6.95 (m, 7H), 2.26 (s, 3H), 2.24 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 194.39, 189.49, 146.92, 145.41, 144.37, 143.20, 138.74, 137.51, 134.67, 134.58, 134.21, 132.29, 129.78, 129.75, 129.71, 129.00, 128.97, 128.78, 128.65, 128.50, 127.70, 127.60, 21.57, 21.49. m.p. 177 - 179 °C. **HRMS** (ESI) calcd for C₃₂H₂₄O₂SNa [M + Na]⁺: 495.1389, found: 495.1382.

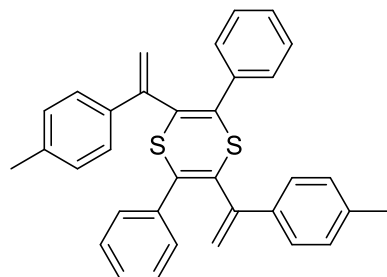
Procedure for preparation of **8**¹²: To an oven-dried 10 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, **3a** (0.2 mmol, 1.0 equiv., 100.9 mg) are diluted in dry THF (2 mL) at 0 °C. methylmagnesium bromide solution (3.0 M in THF, 0.27 mL, 0.8 mmol) was added to the reaction vessel, and the reaction was stirred for 2 h at 0 °C under N₂ atmosphere. Upon the completion of reaction monitored by TLC, and the reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were washed with brine (10 mL), dried

over MgSO₄, and concentrated under reduced pressure, the pure product was isolated by column chromatography on silica gel (PE: EA = 7: 1, v: v) as white solid. (78.4 mg, 73%)



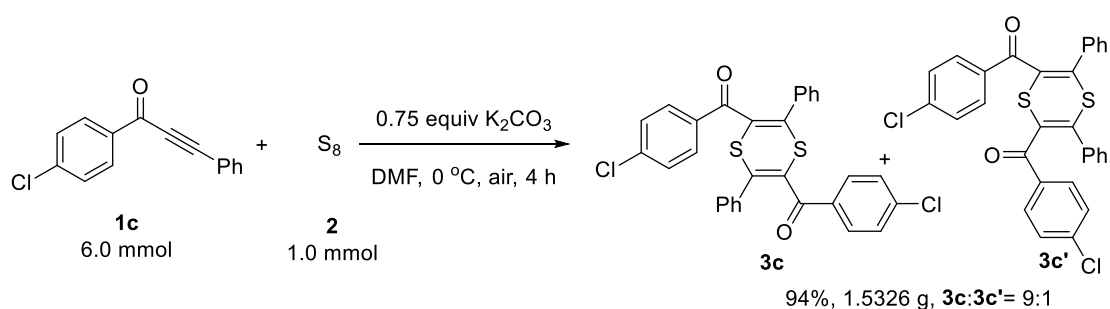
¹H NMR (500 MHz, CDCl₃) δ 7.26-7.17 (m, 10 H), 7.13-7.11 (m, 4H), 6.96-6.93 (m, 4H), 2.55 (s, 2H), 2.36 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 145.41, 143.64, 138.49, 137.45, 137.08, 128.83, 128.14, 127.91, 125.35, 78.36, 30.13, 21.03. m.p. 78 - 80 °C. HRMS (ESI) calcd for C₃₄H₃₂O₂S₂Na [M + Na]⁺: 559.1736, found: 559.1731.

Procedure for preparation of **9**¹³: To an oven-dried 10 mL Schlenk tube charged with a PTFE-coated magnetic stirring bar, Ph₃PMeBr (4.0 equiv., 142.9 mg, 0.4 mmol) was added. Under nitrogen atmosphere, 2 mL of tetrahydrofuran and of *t*-BuOK (4.0 equiv., 44.9 mg, 0.4mmol) were added at 0 °C. After 1 h, **3a** (1.0 equiv., 0.1 mmol, 50.5 mg) was added at 80 °C for 4 h. Upon the completion of reaction monitored by TLC, and the reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, and concentrated under reduced pressure, the pure product was isolated by column chromatography on silica gel (PE: EA = 10: 1, v: v) as white solid. (29.0 mg, 58%).



¹H NMR (500 MHz, CDCl₃) δ 7.36-7.34 (m, 4H), 7.32-7.29 (m, 4H), 7.15-7.12 (m, 10H), 5.58 (m, 2H), 5.14 (s, 2H), 2.35 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 145.22, 140.13, 138.11, 137.22, 135.52, 134.60, 129.27, 129.17, 127.92, 127.85, 126.44, 116.65, 21.19. m.p. 118 - 120 °C. HRMS (ESI) calcd for C₃₄H₂₉S₂ [M + H]⁺: 501.1705, found: 501.1709.

3.5 Gram-scale experiment

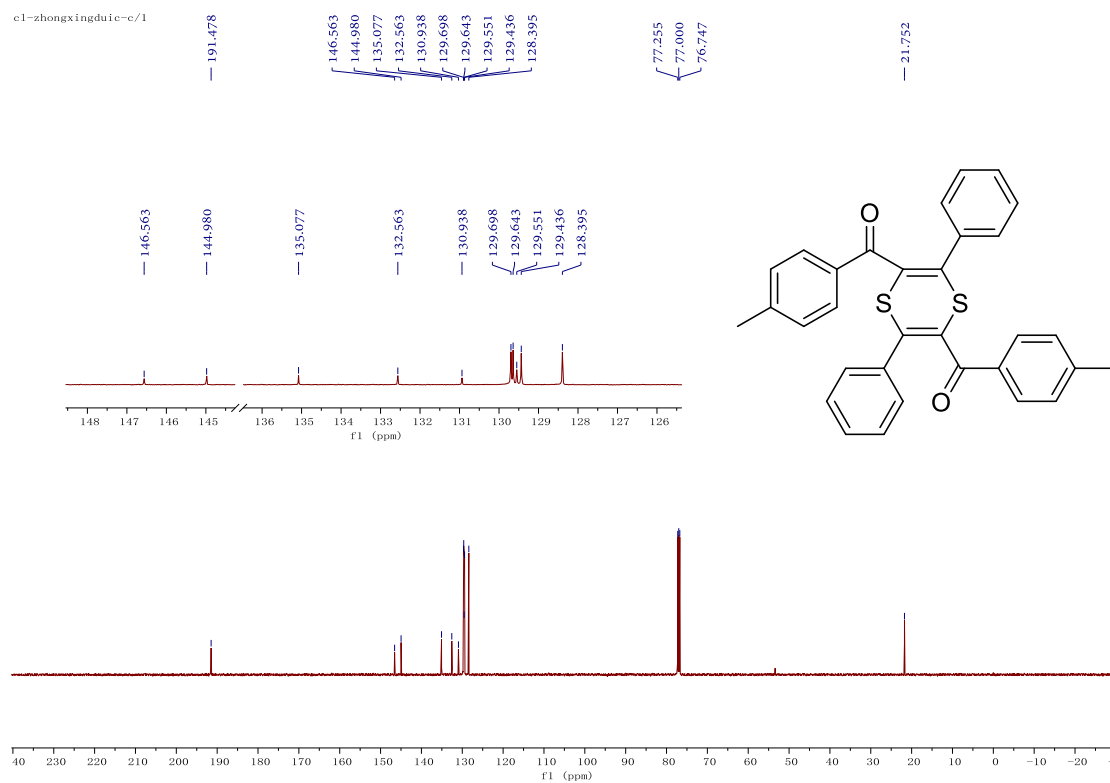
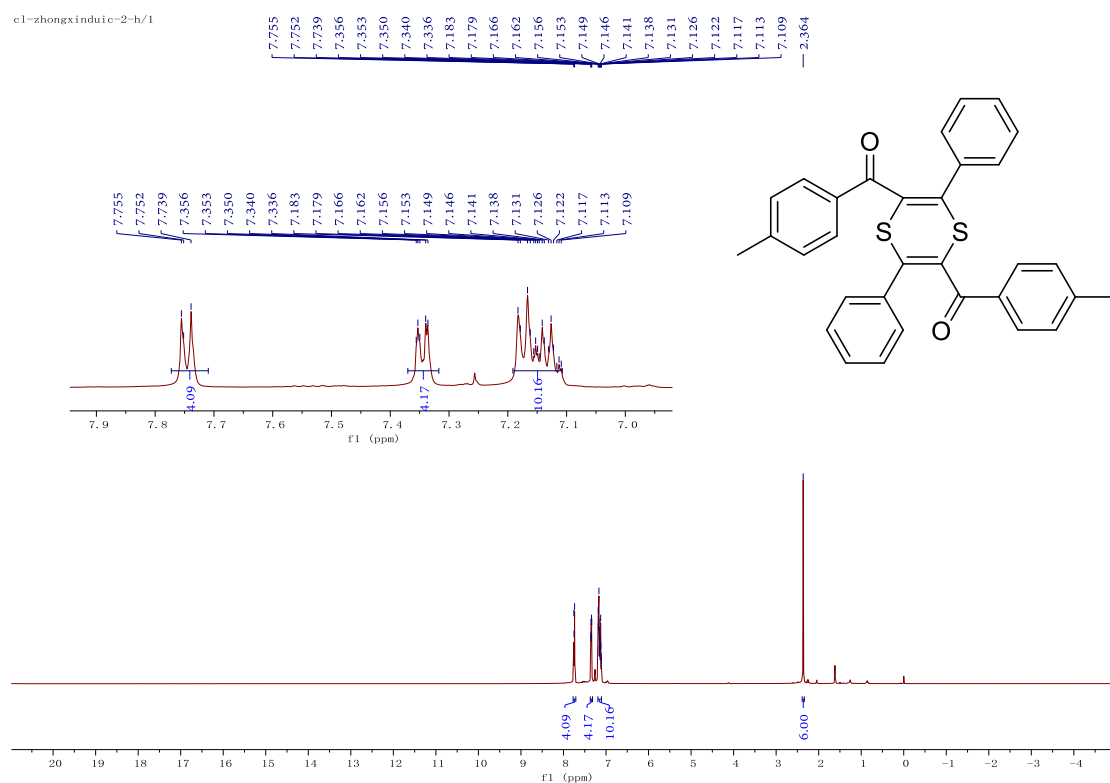


In a schlenk tube **1a** (6.0 mmol, 1.4441 g), **2** (1.0 mmol, 256.5 mg), K₂CO₃ (4.5 mmol, 621.9 mg) and DMF (60.0 mL) were stirred at 0 °C. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) afforded desired compound as a yellow solid (**3c:3c'** = 9:1, 1.5326 g, 94% total yield)

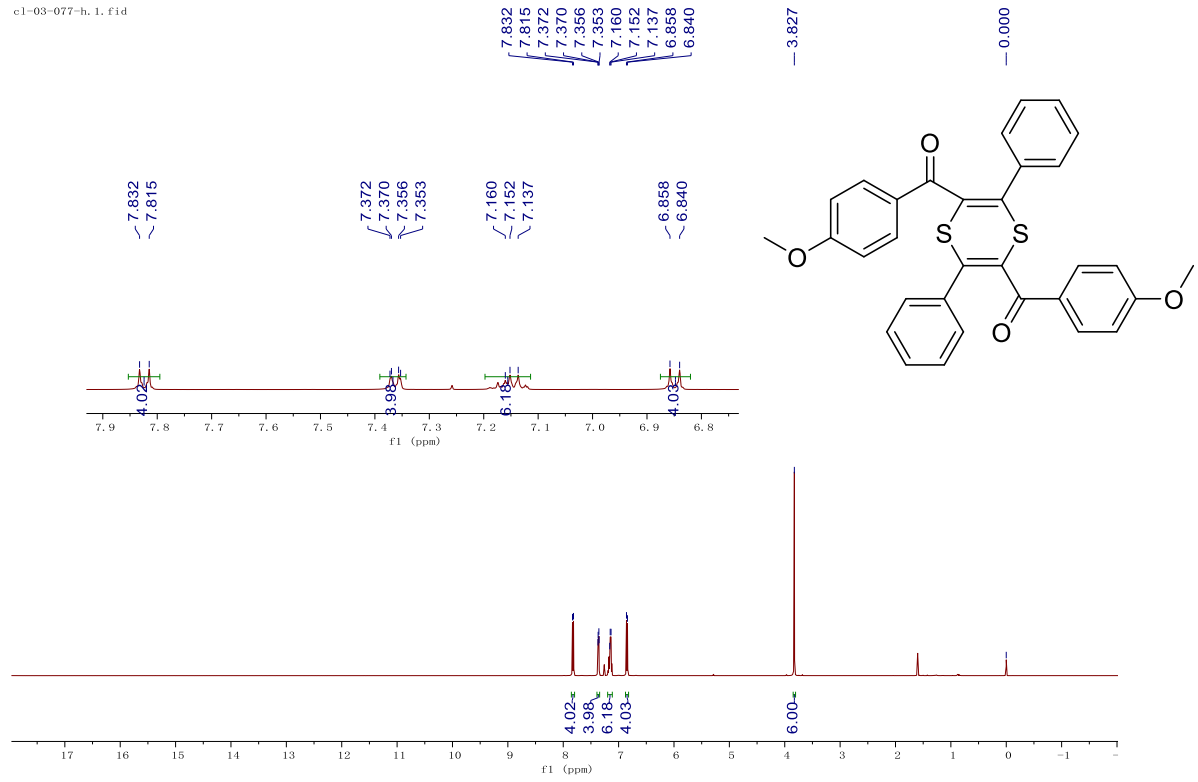
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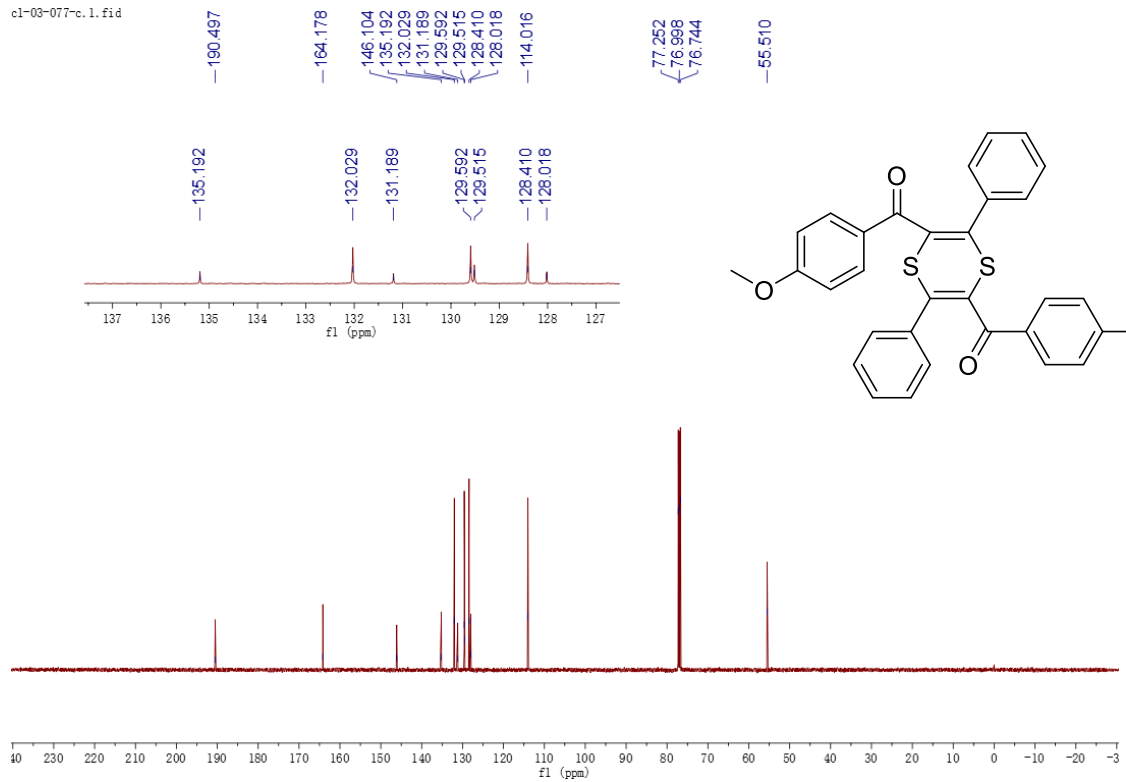
5. Copies of NMR spectra



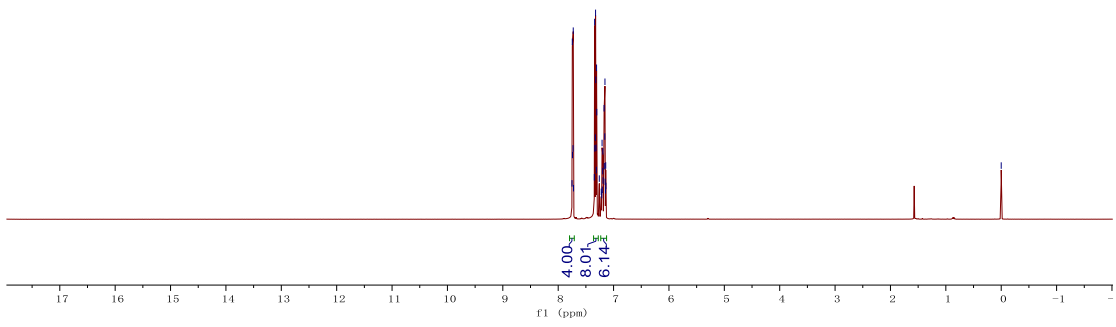
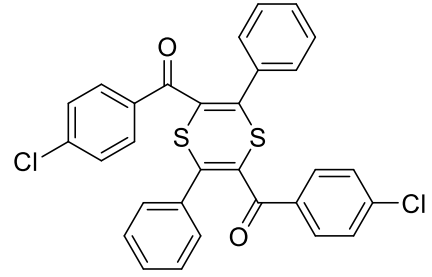
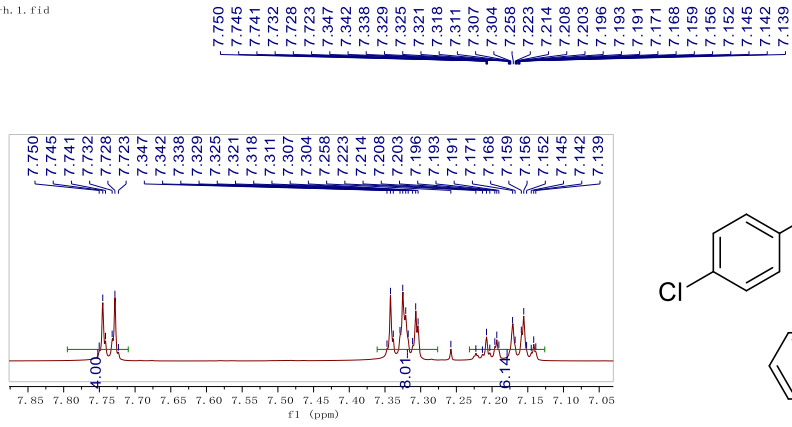
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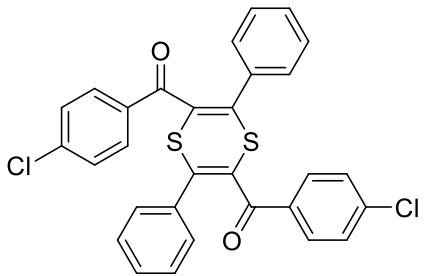
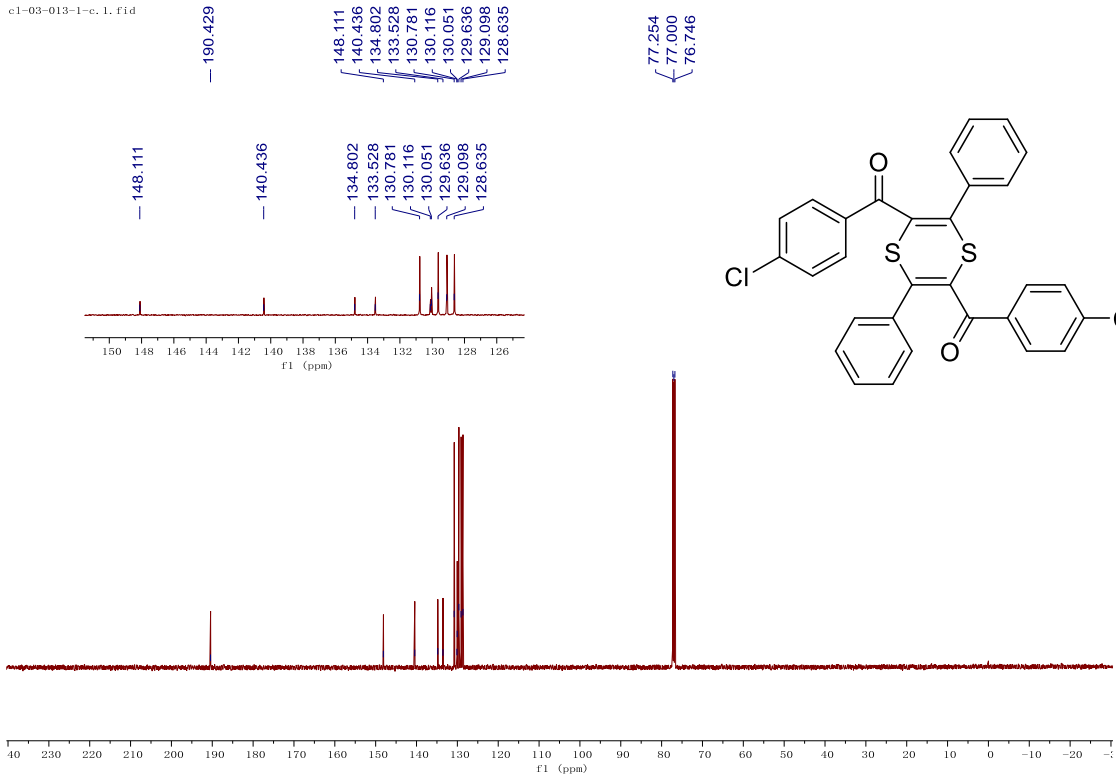
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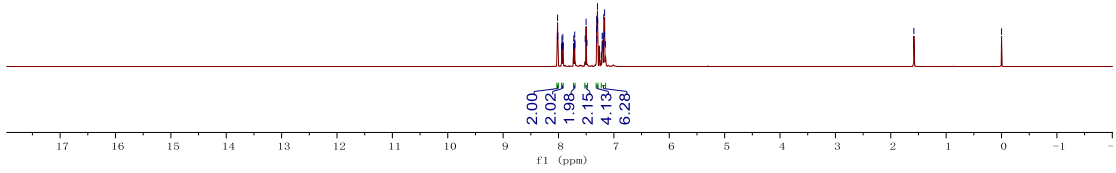
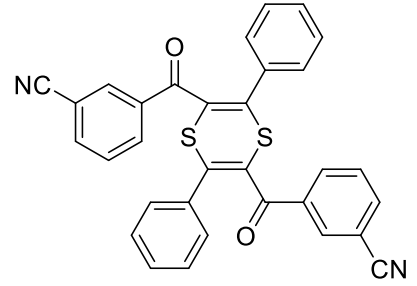
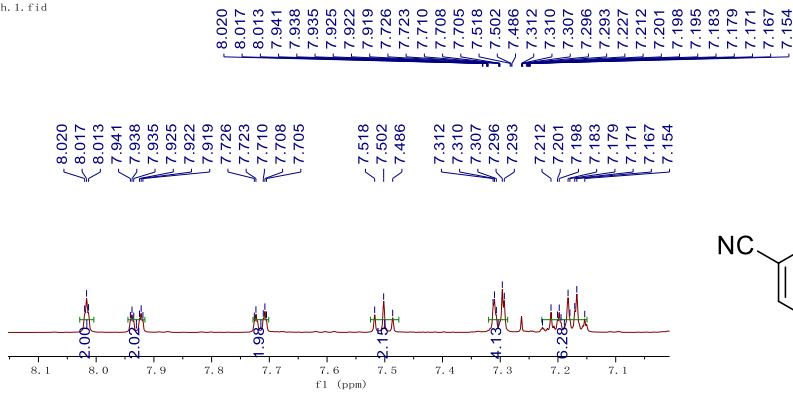
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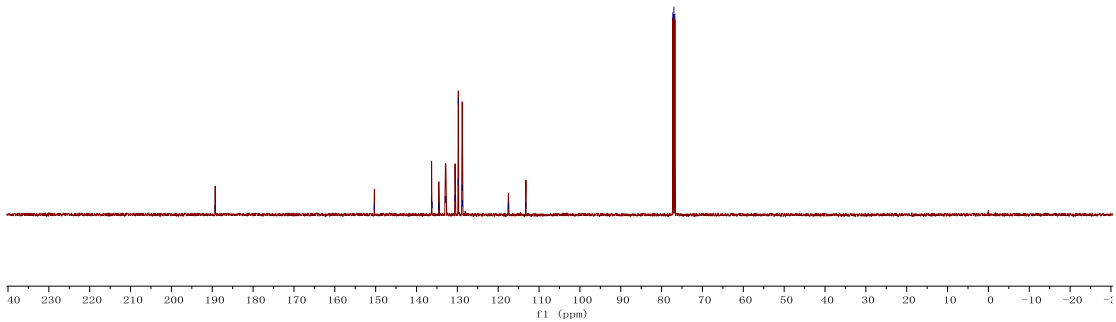
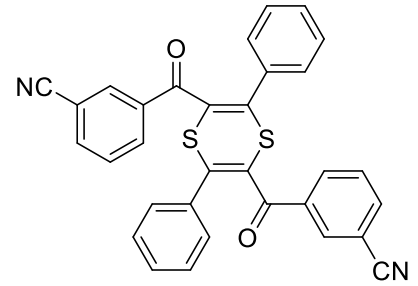
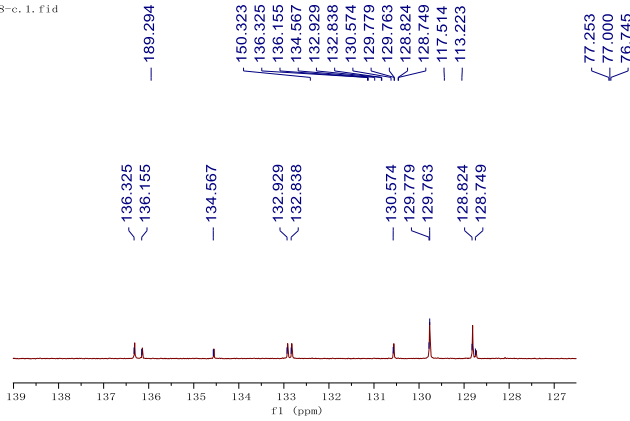
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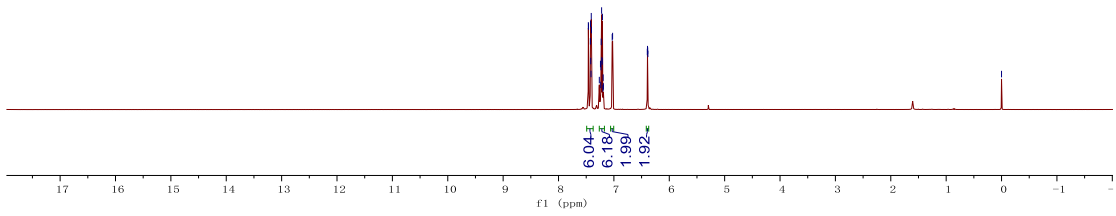
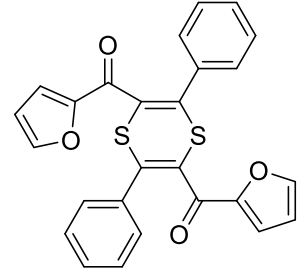
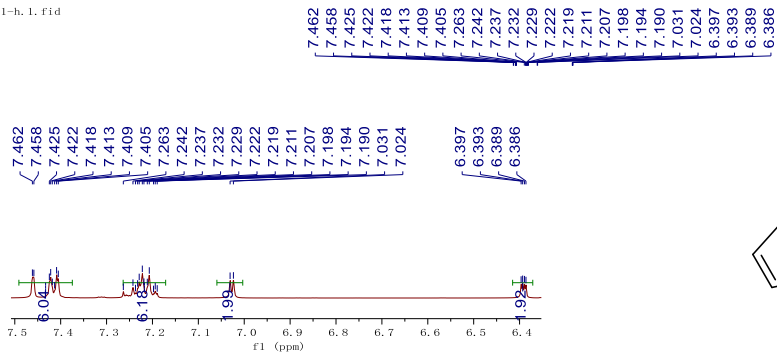
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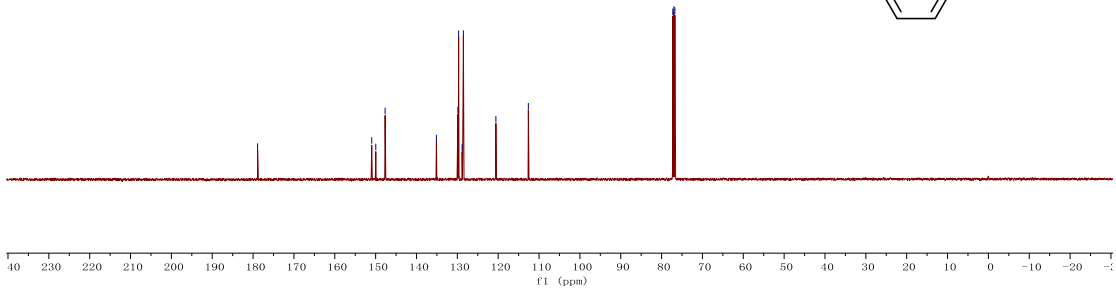
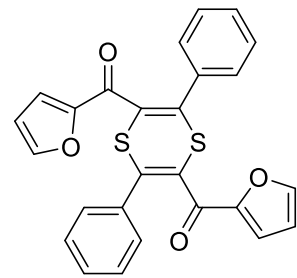
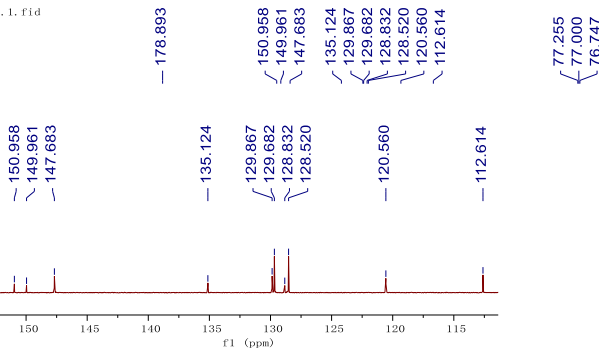
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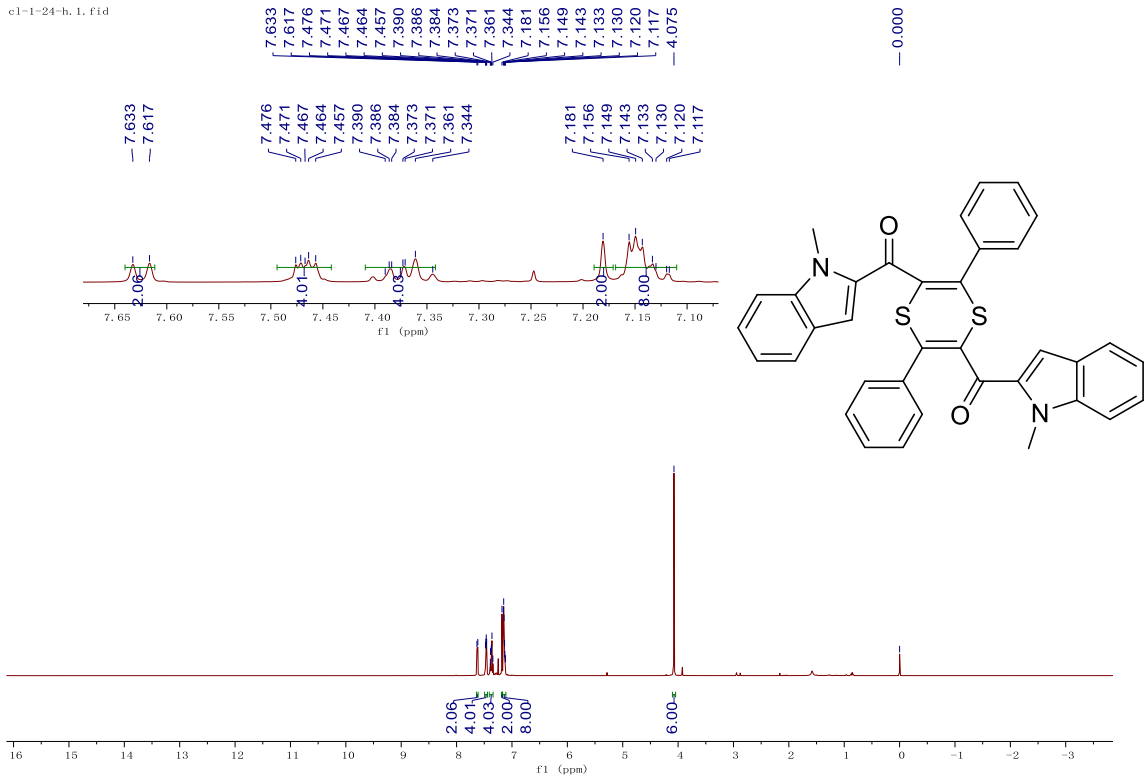
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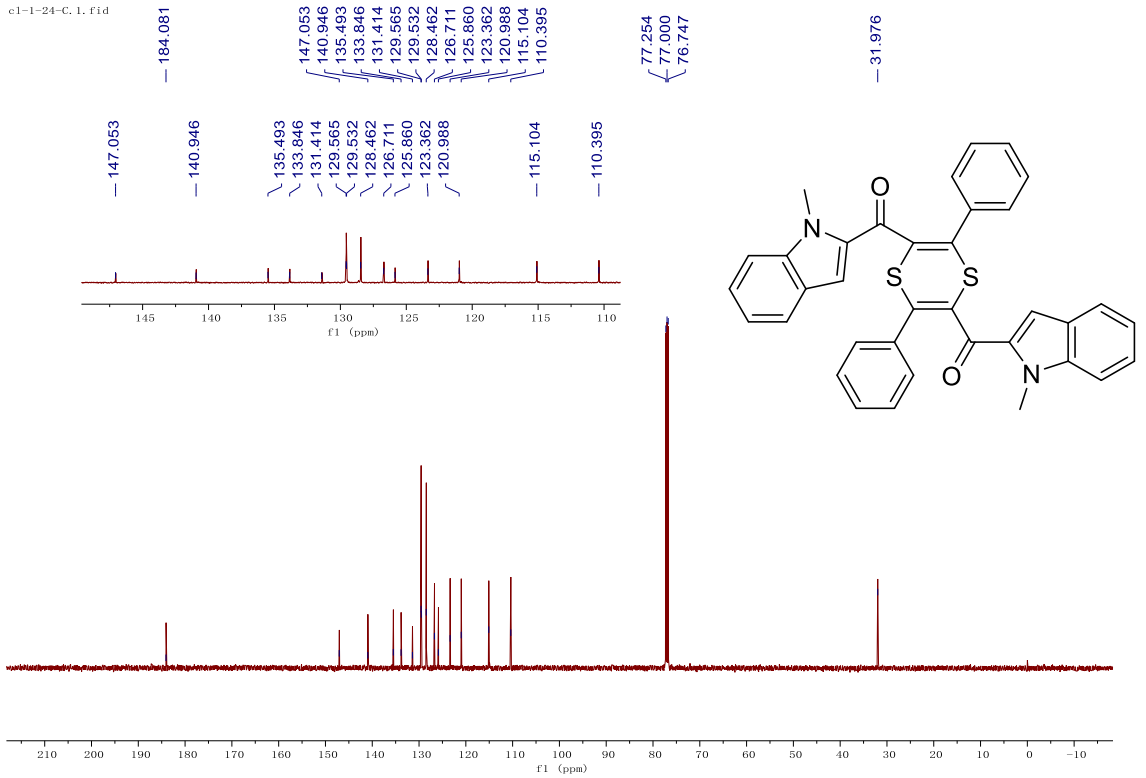
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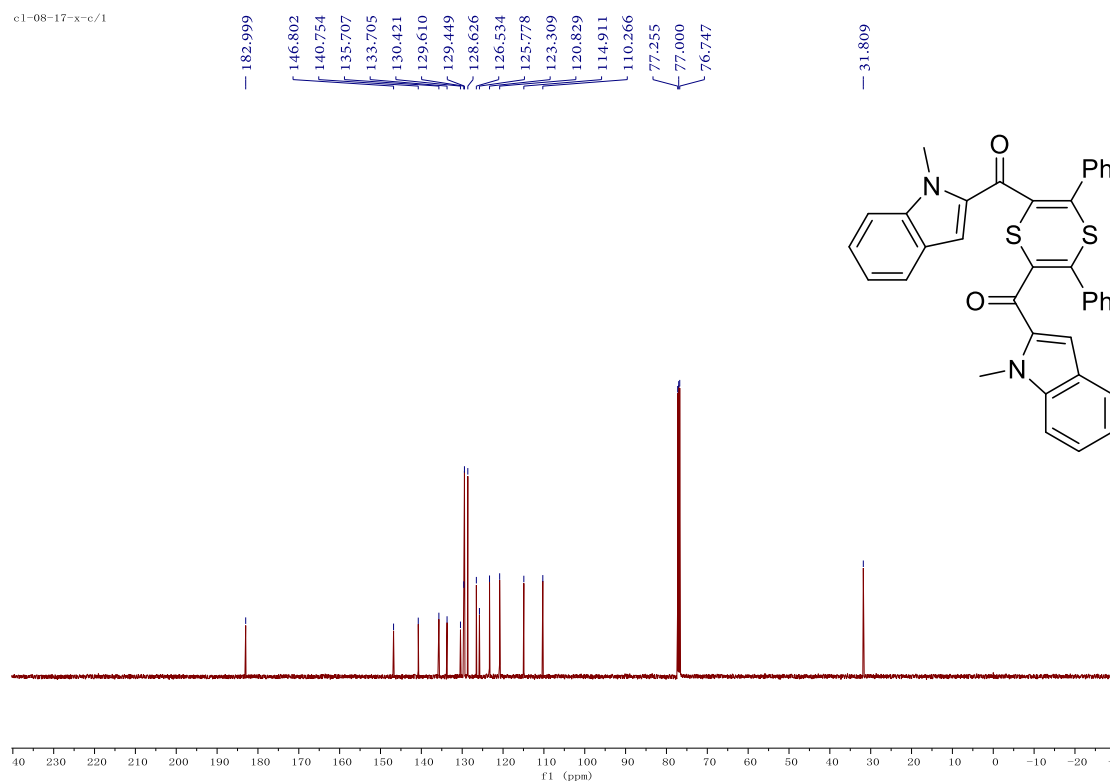
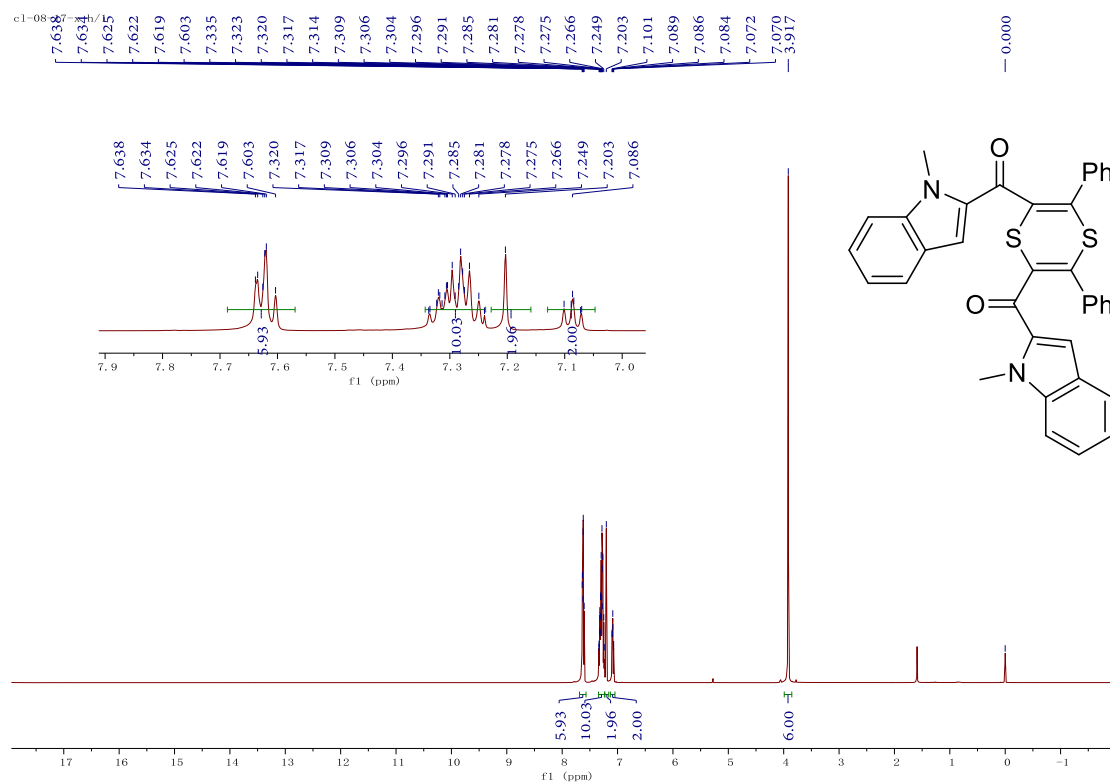


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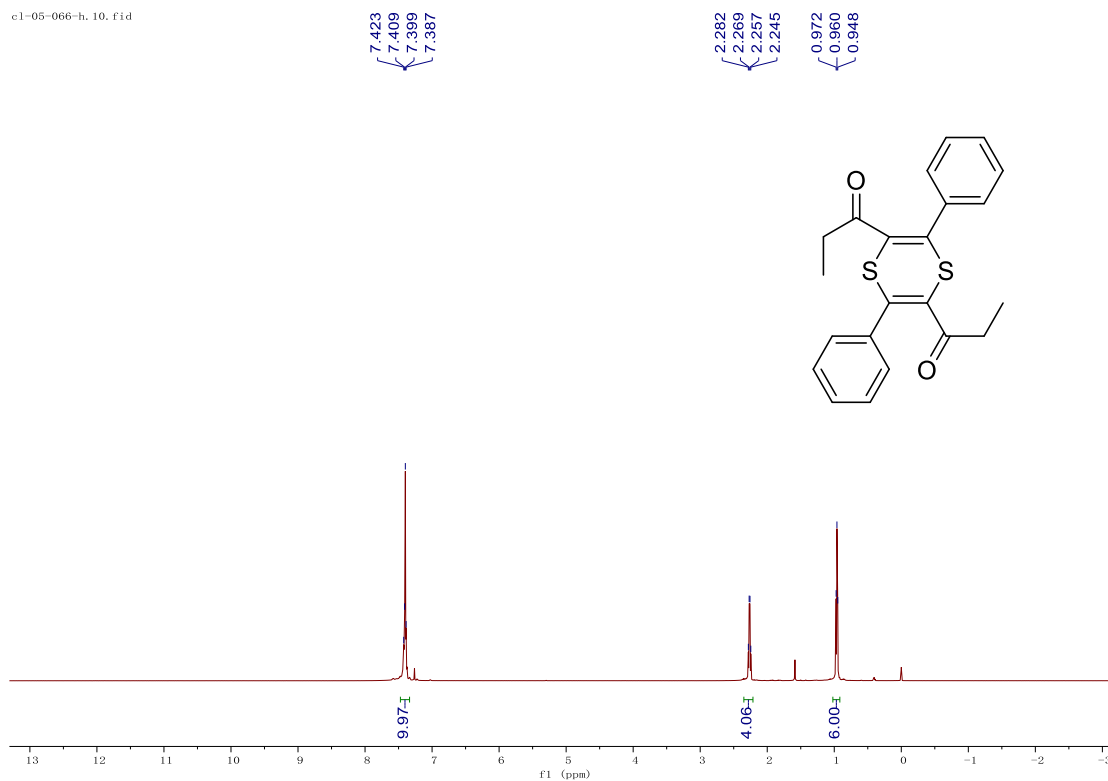


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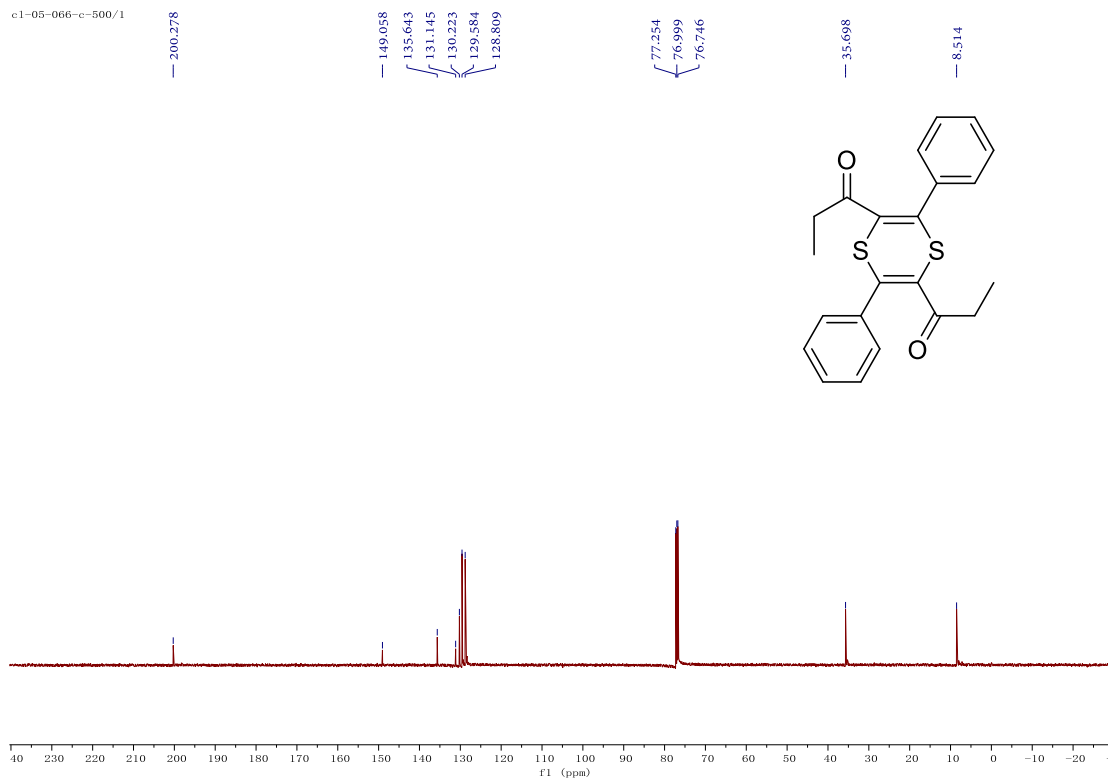




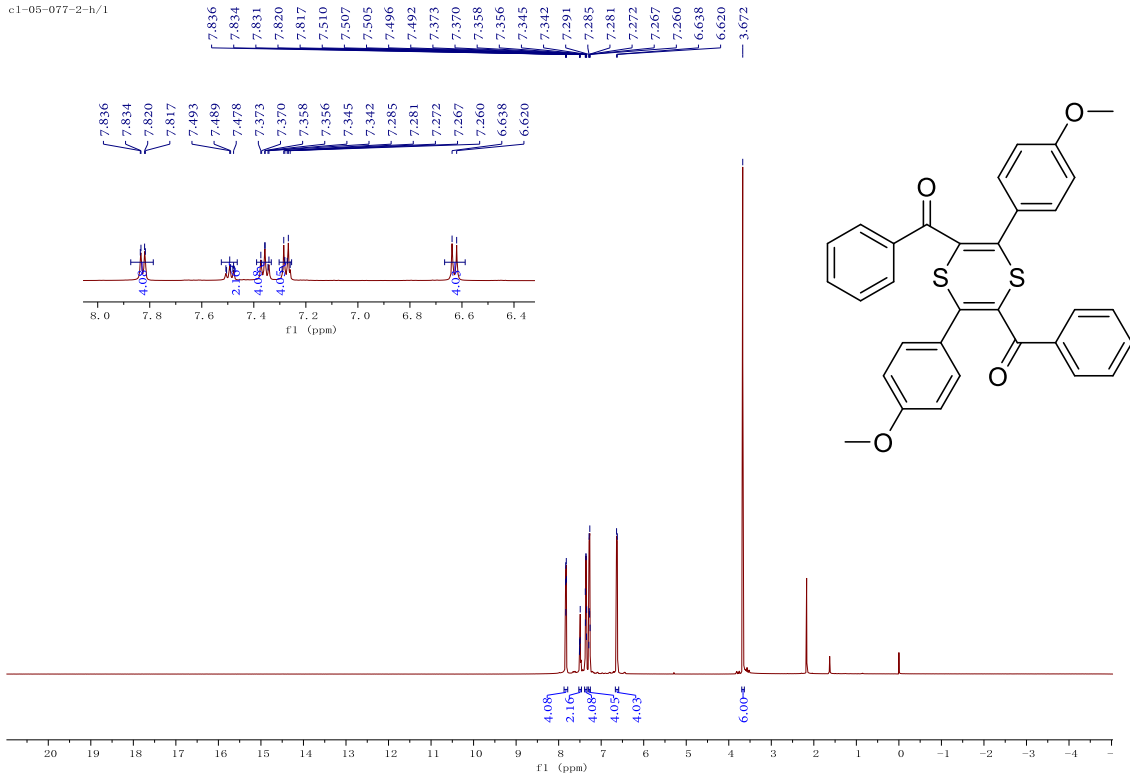
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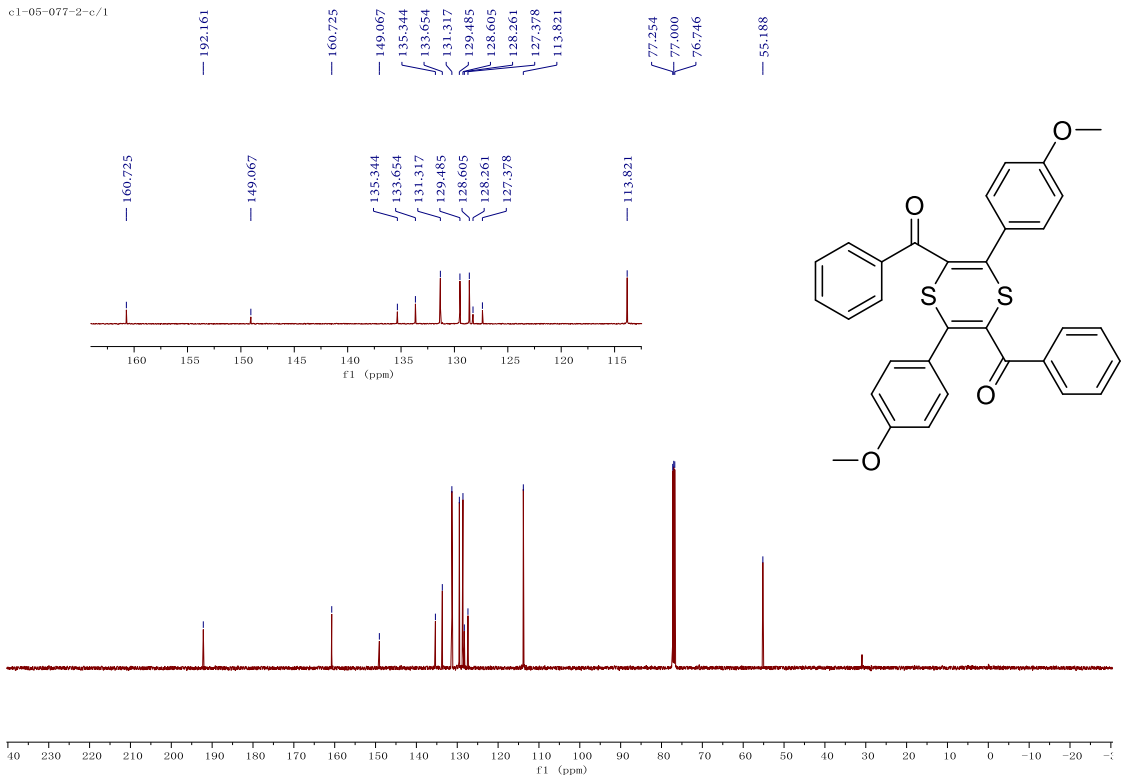
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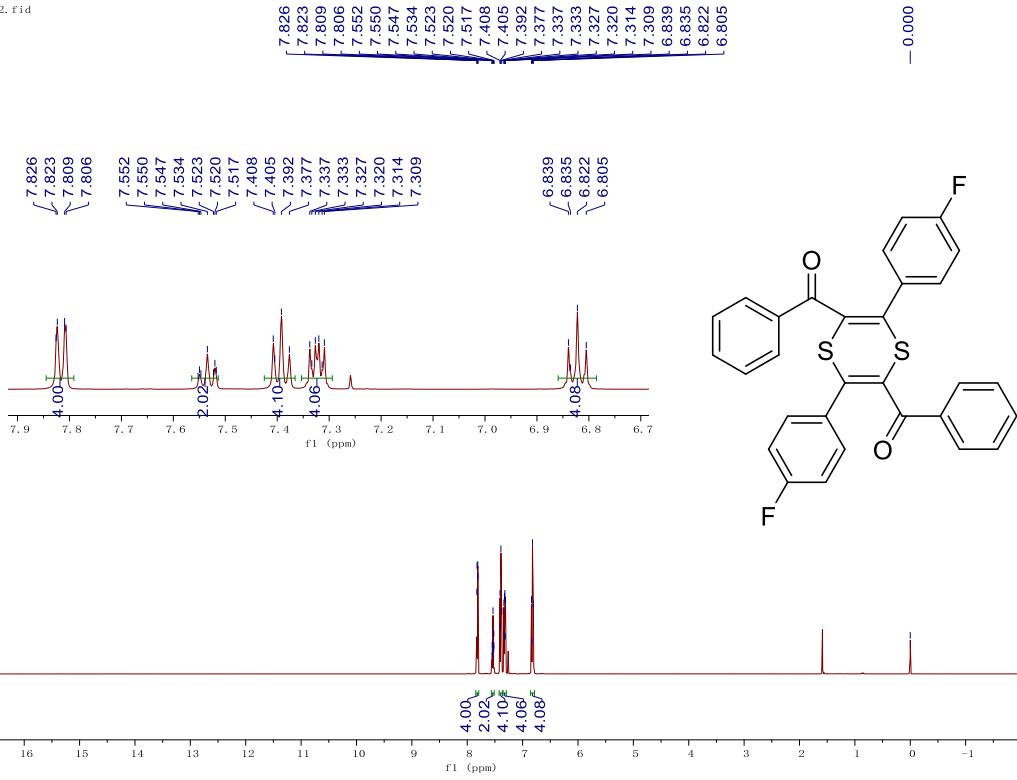
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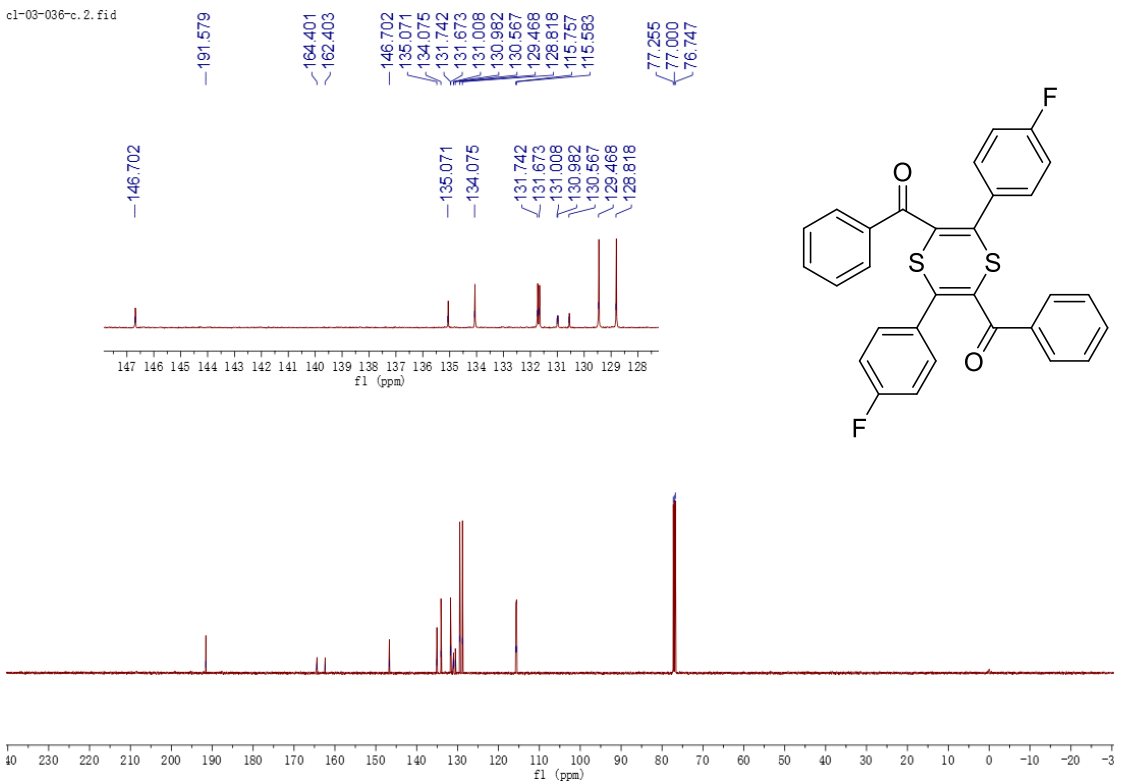
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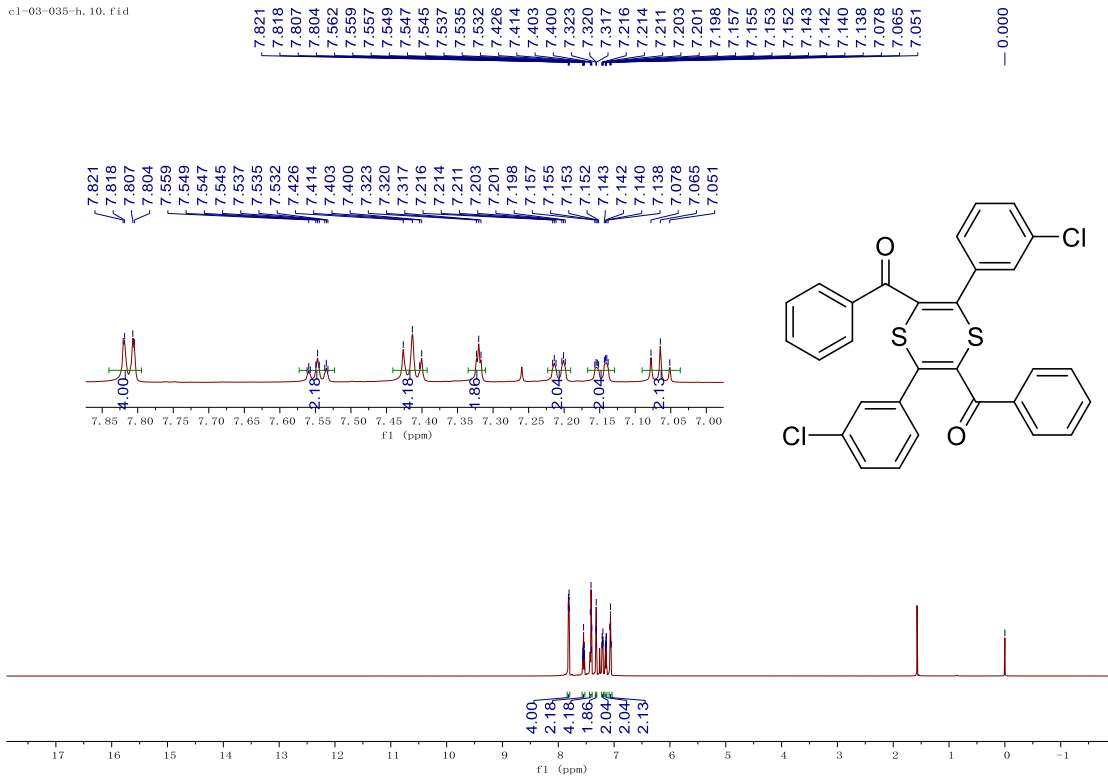
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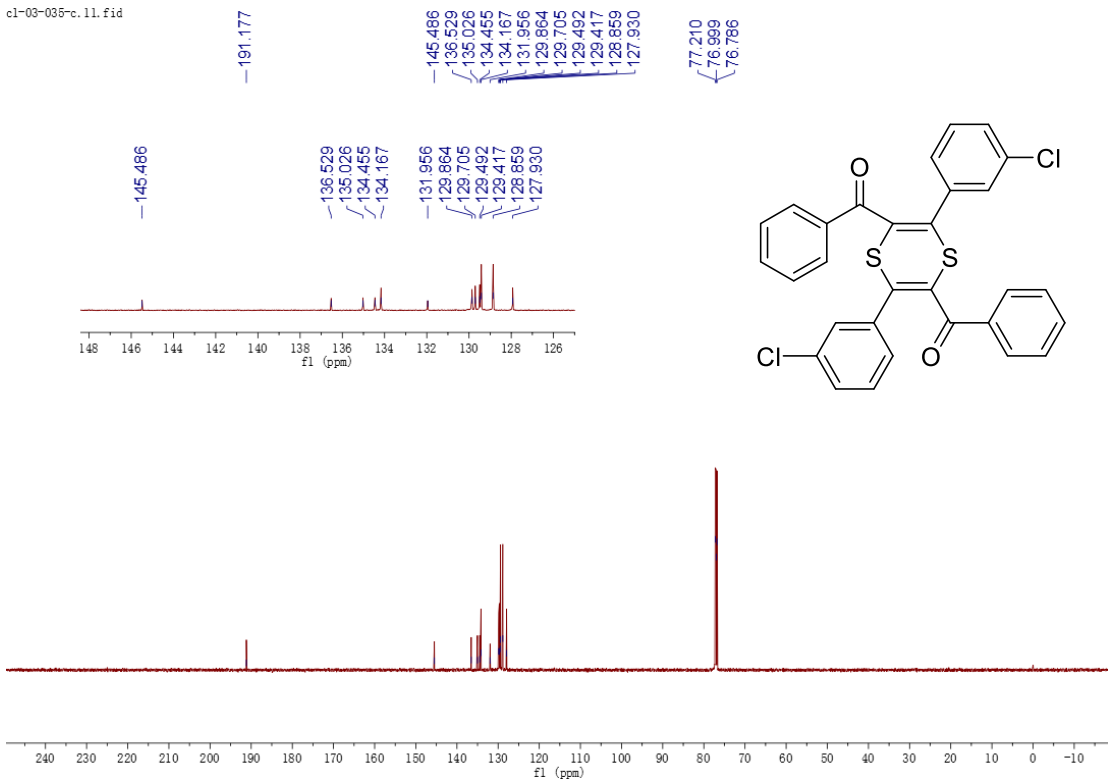
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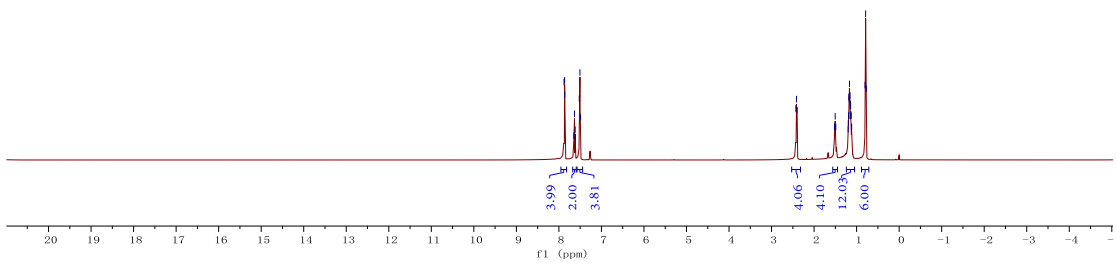
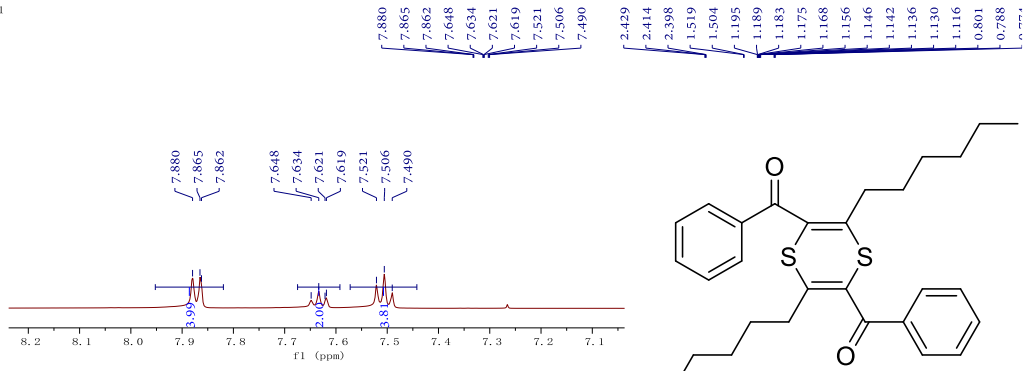
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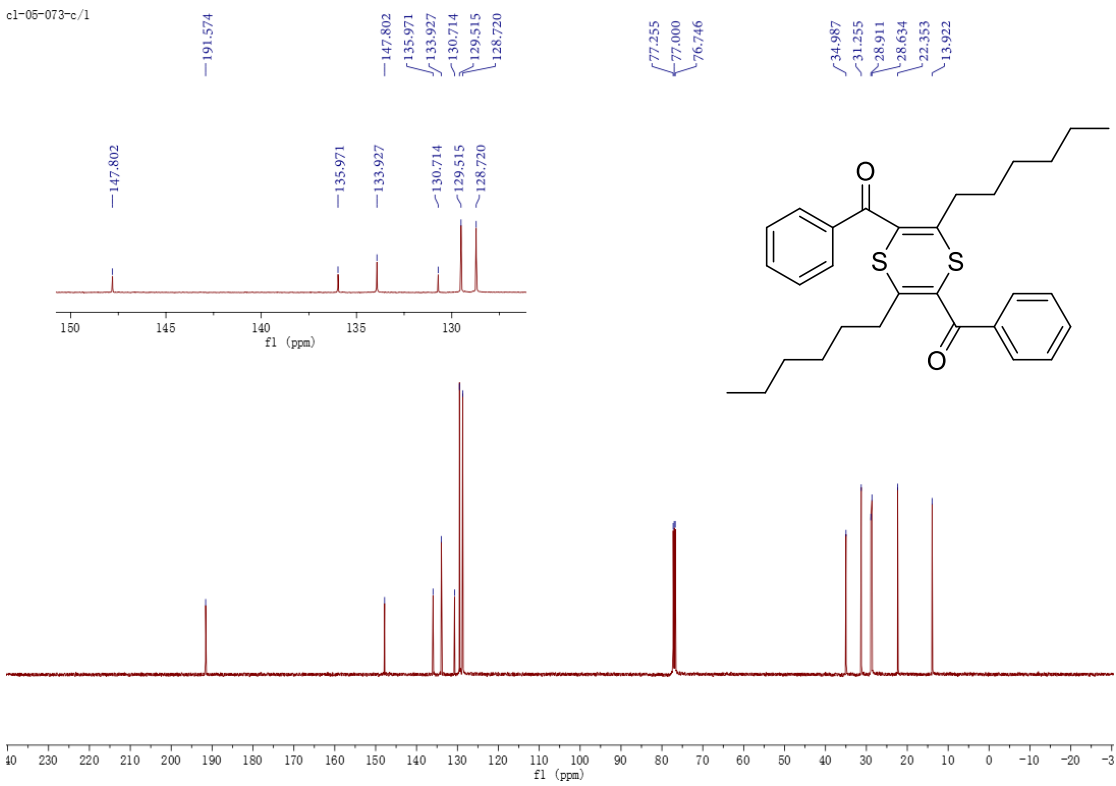
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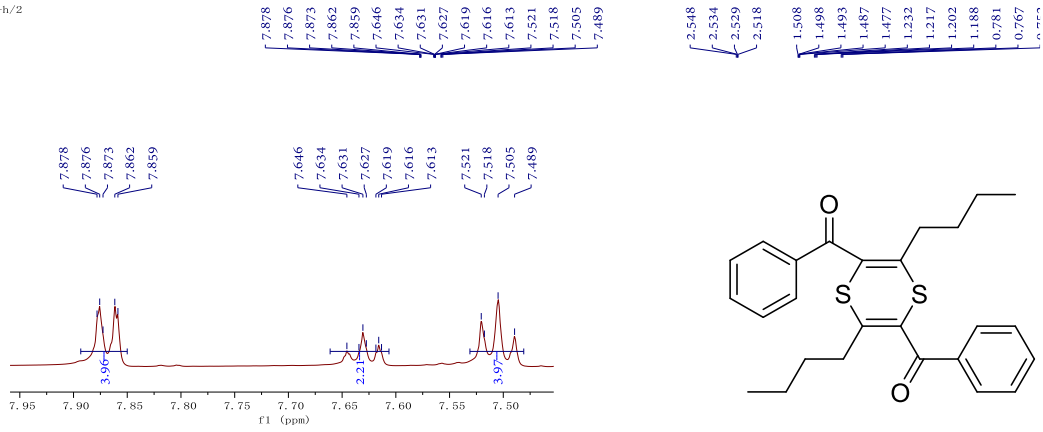
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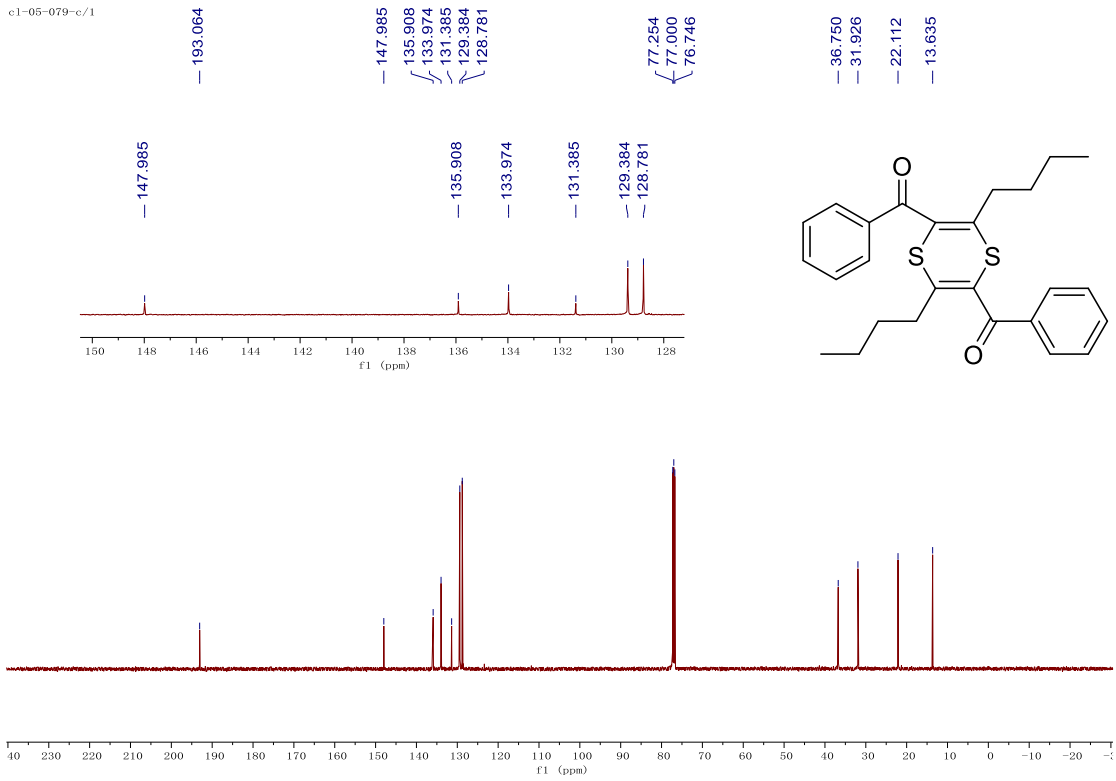
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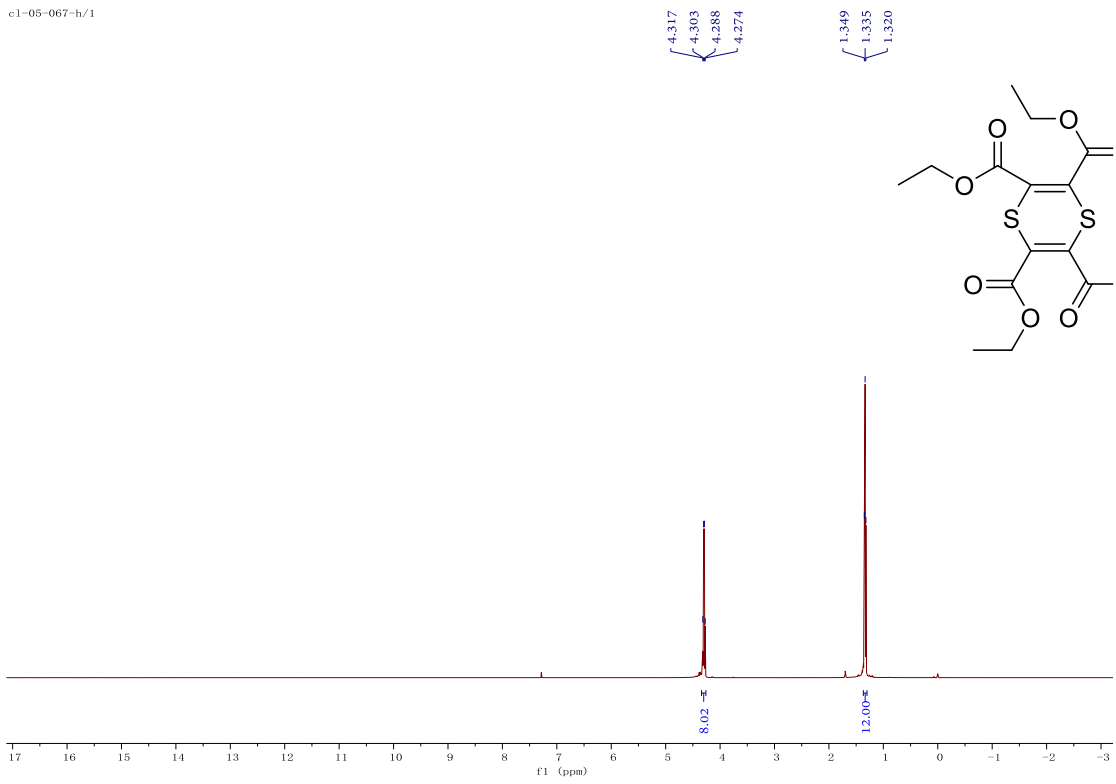
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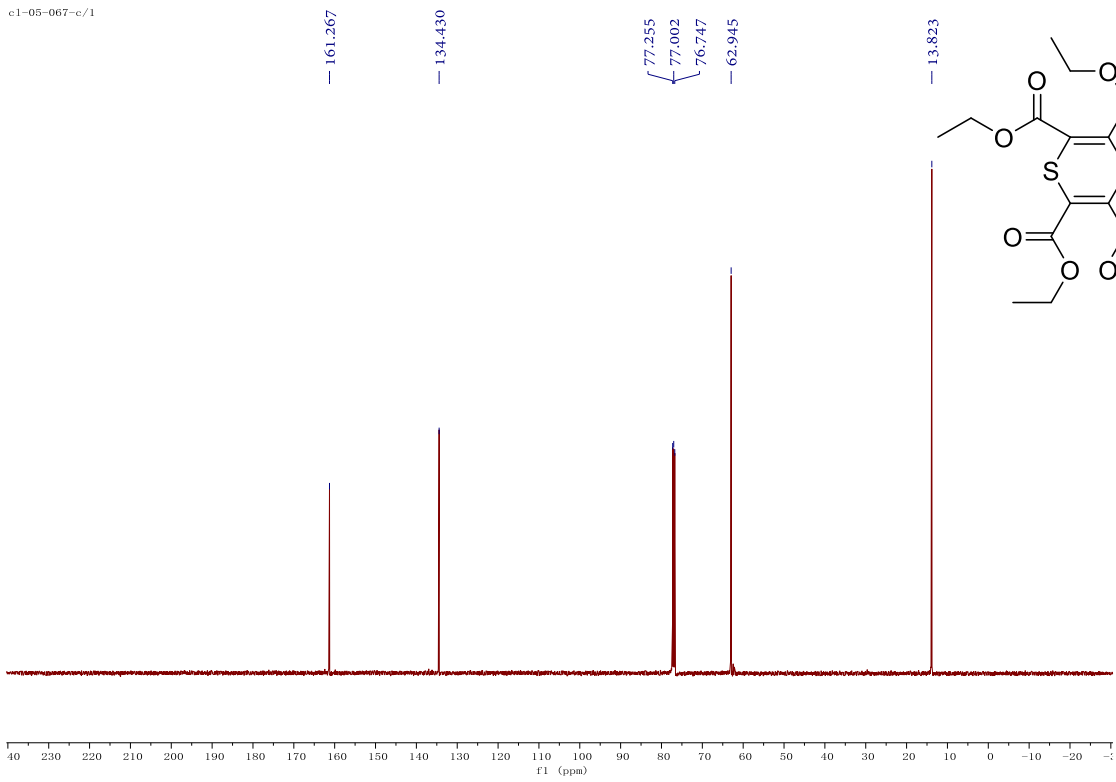
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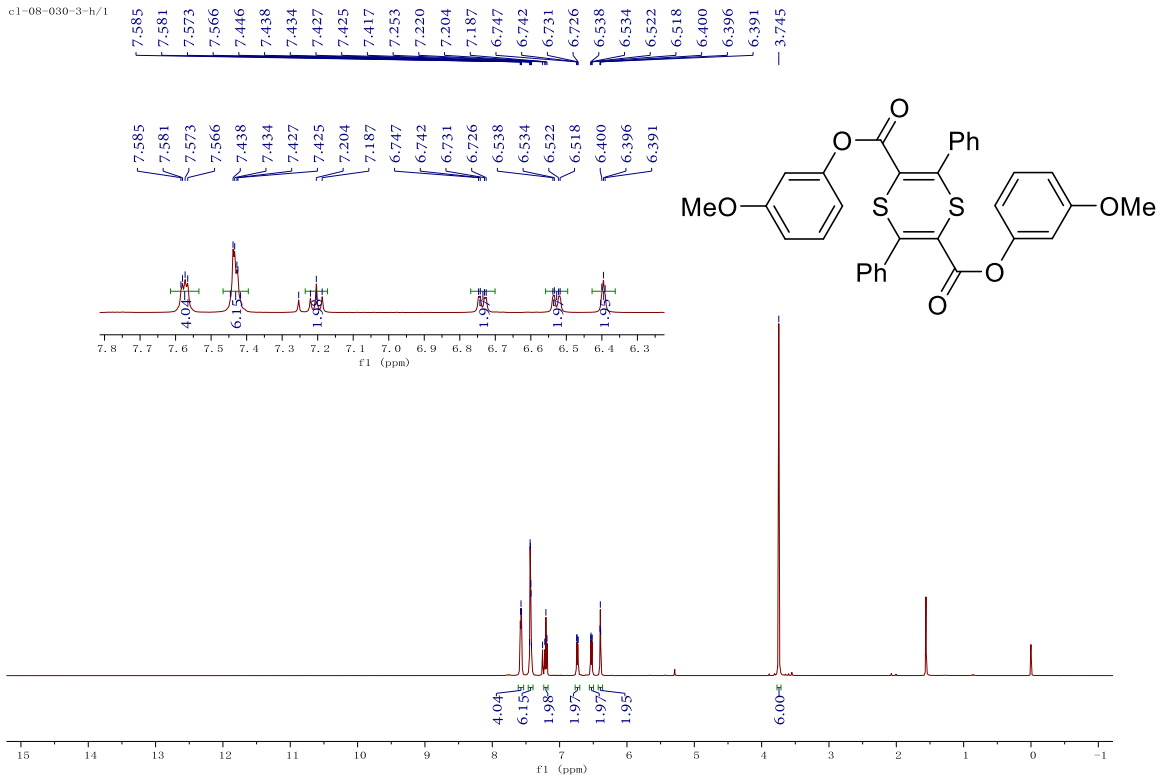
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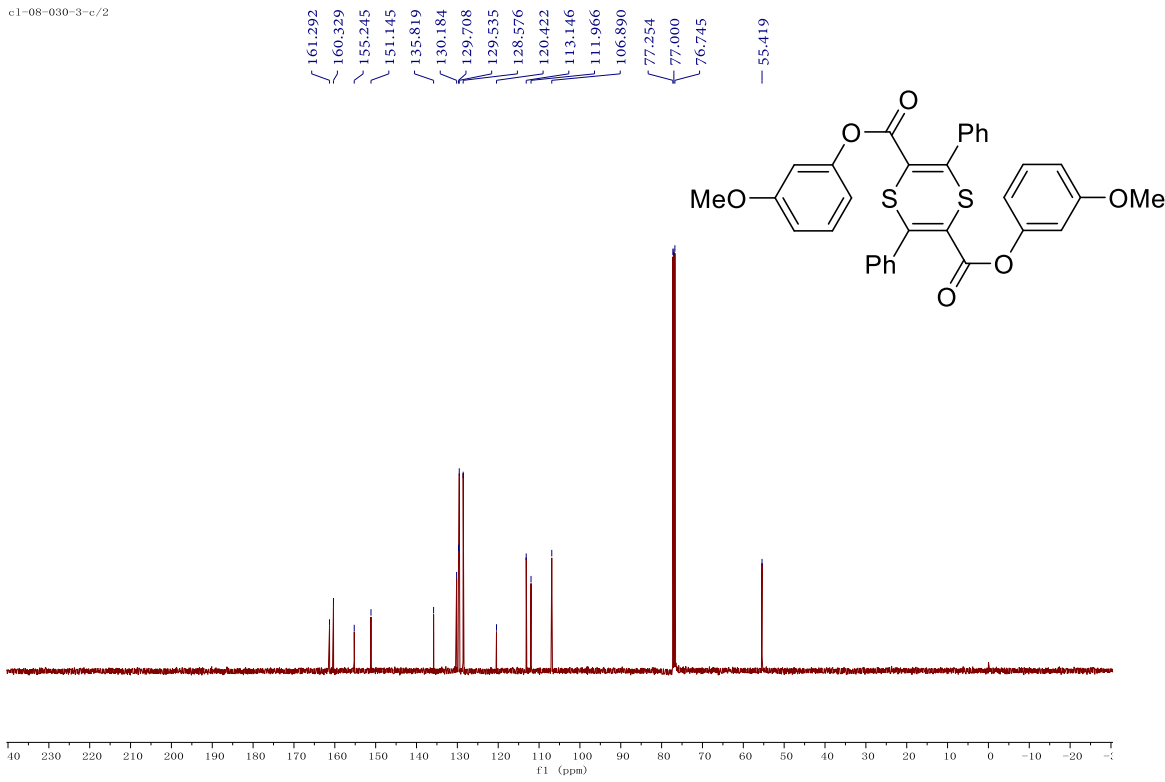
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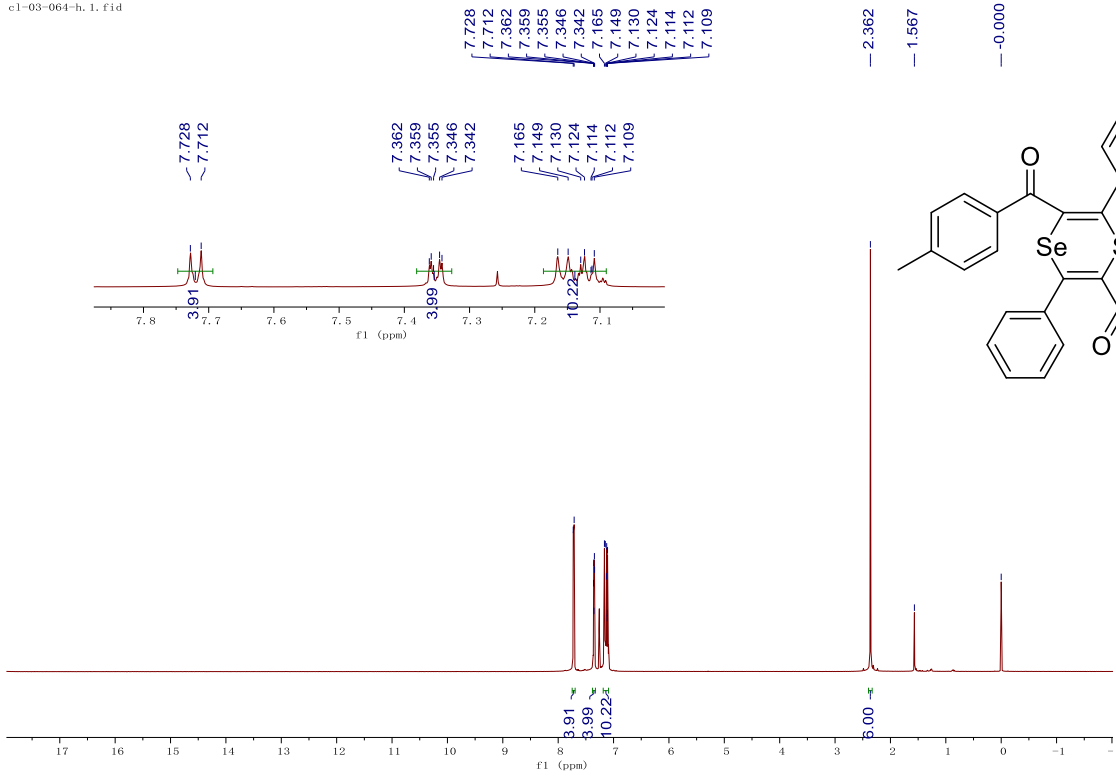
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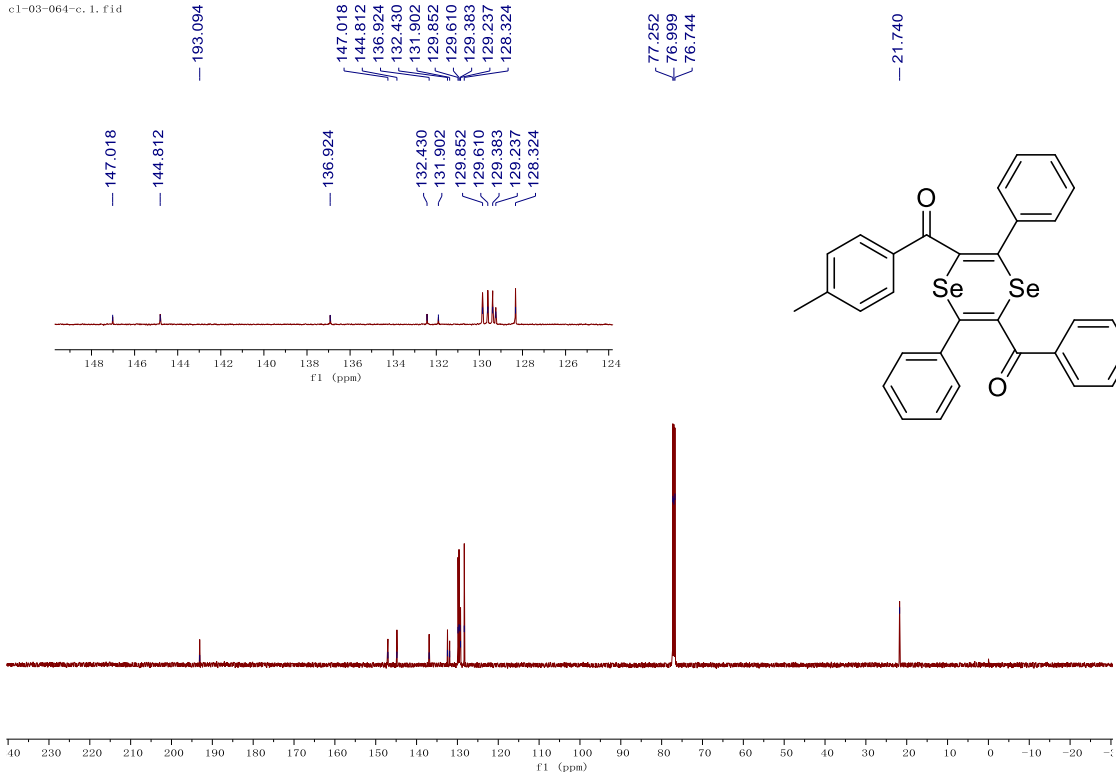
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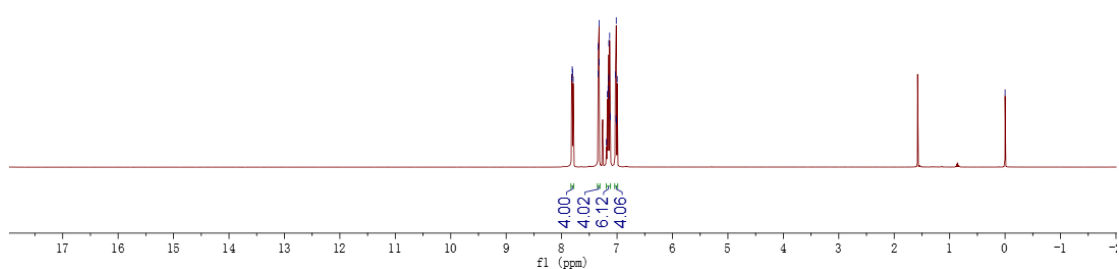
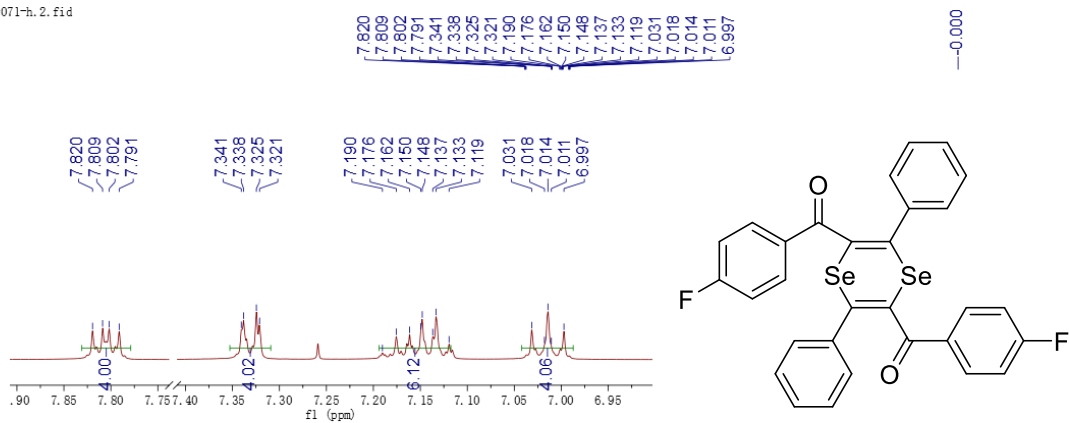
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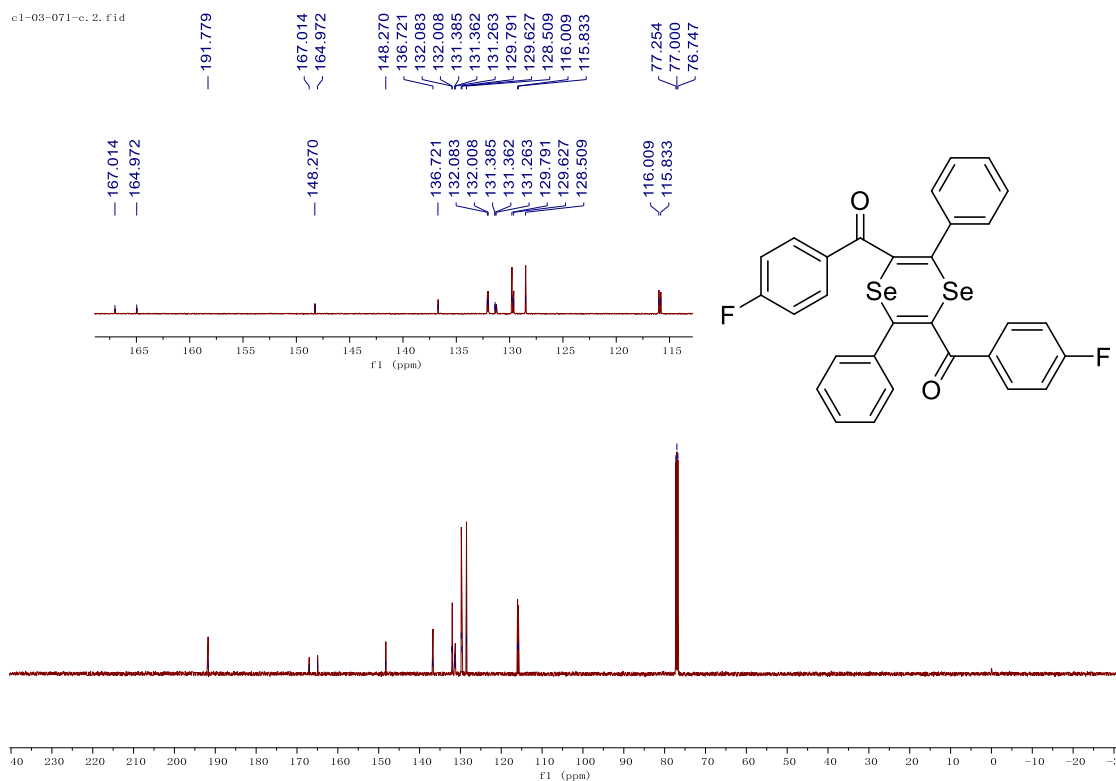
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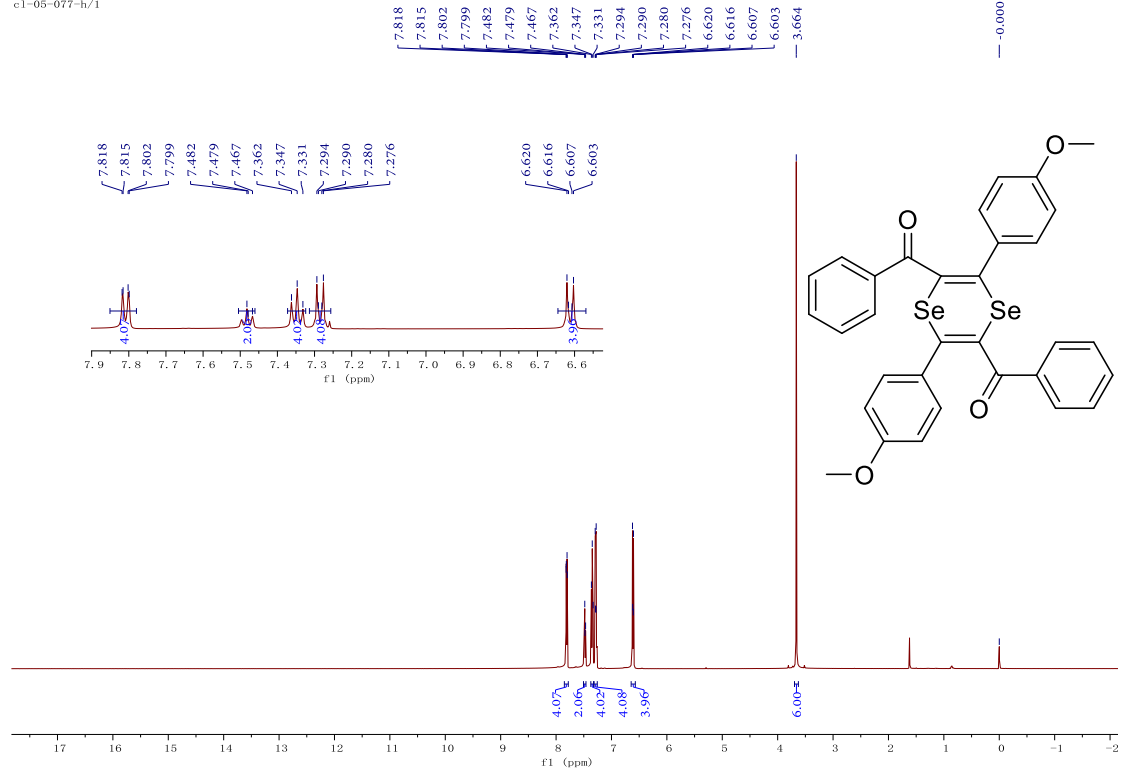
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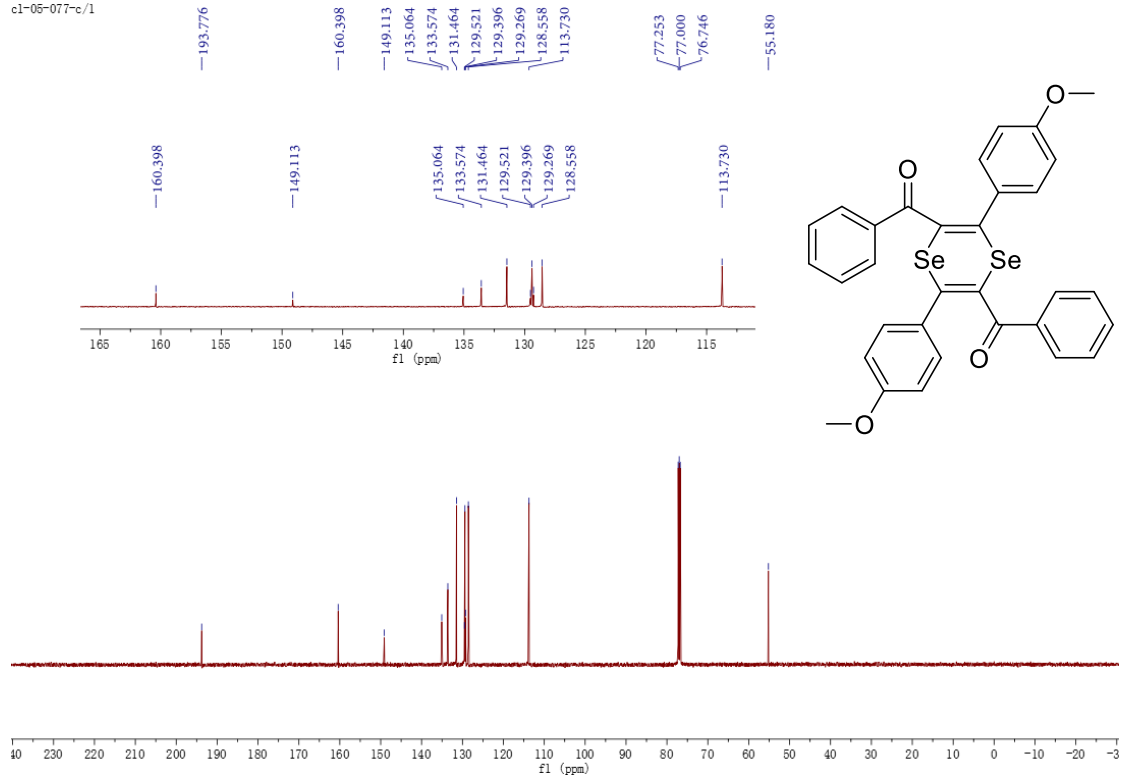
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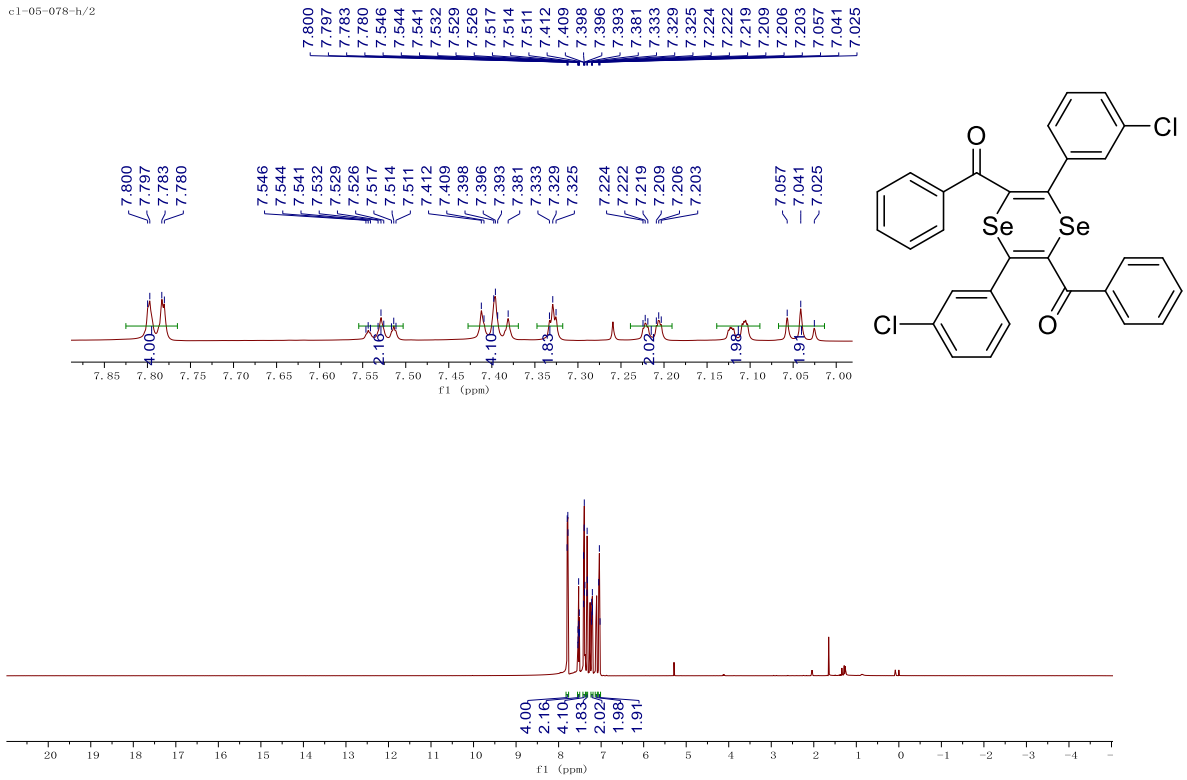
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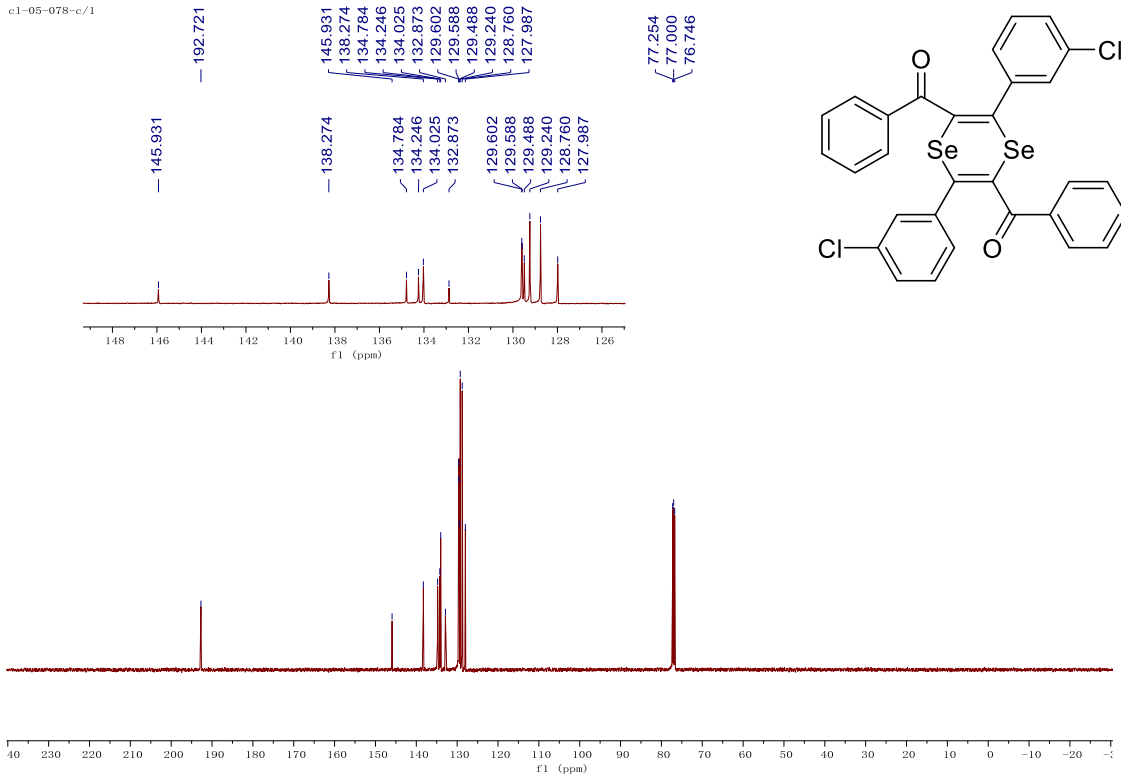
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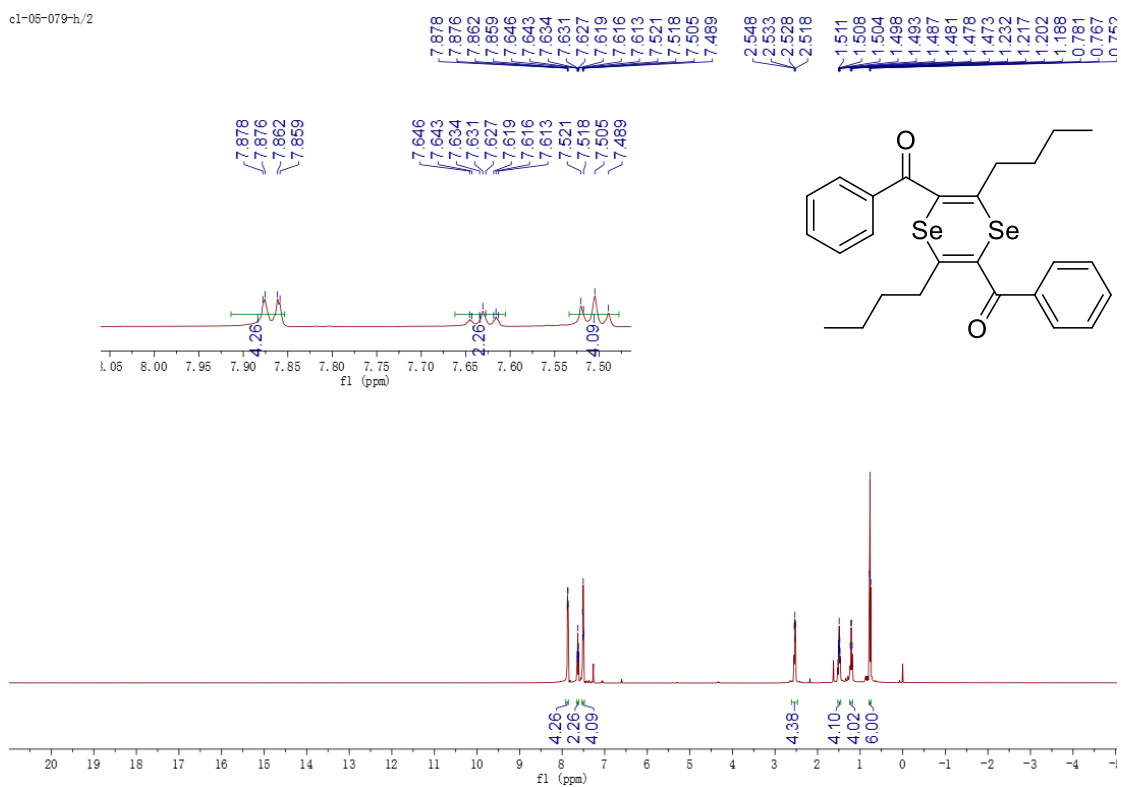
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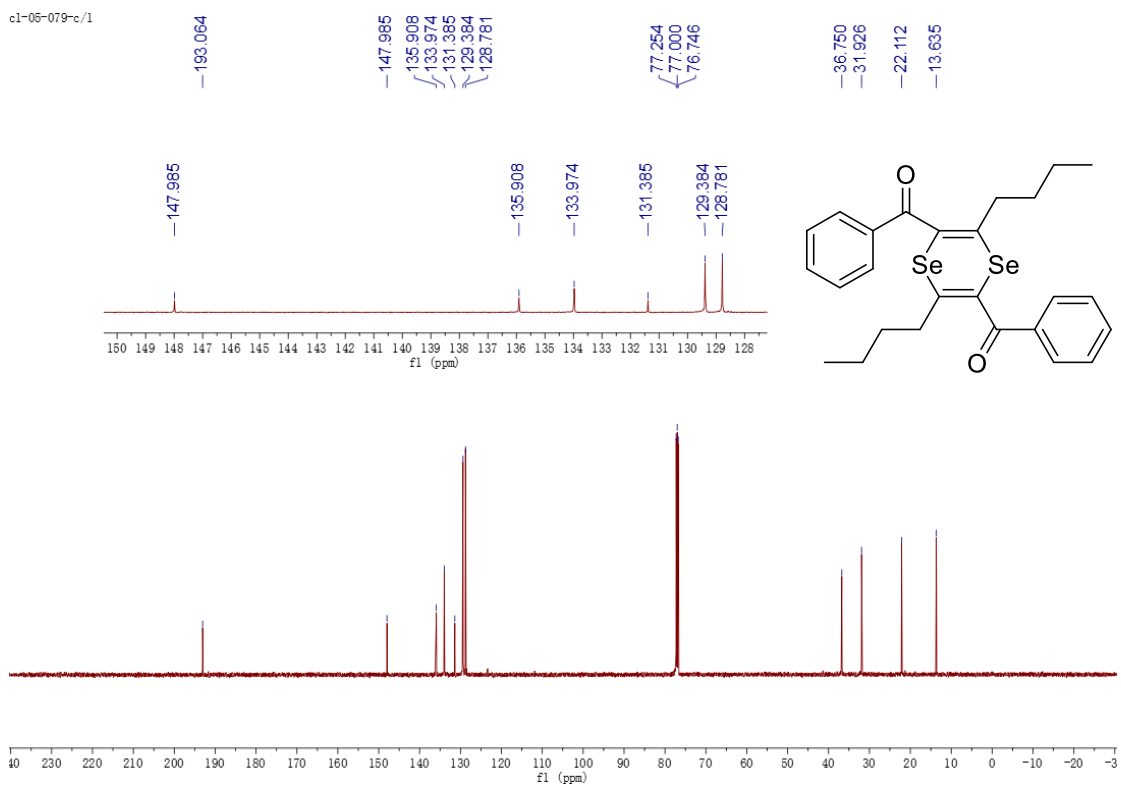
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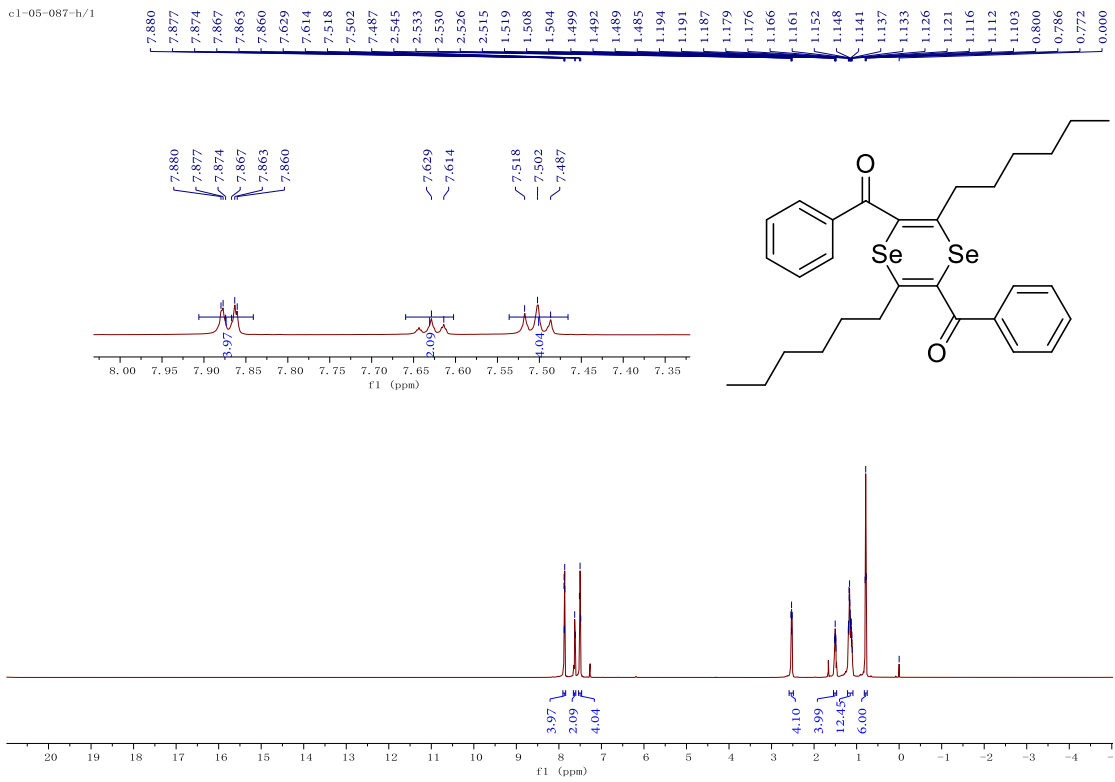
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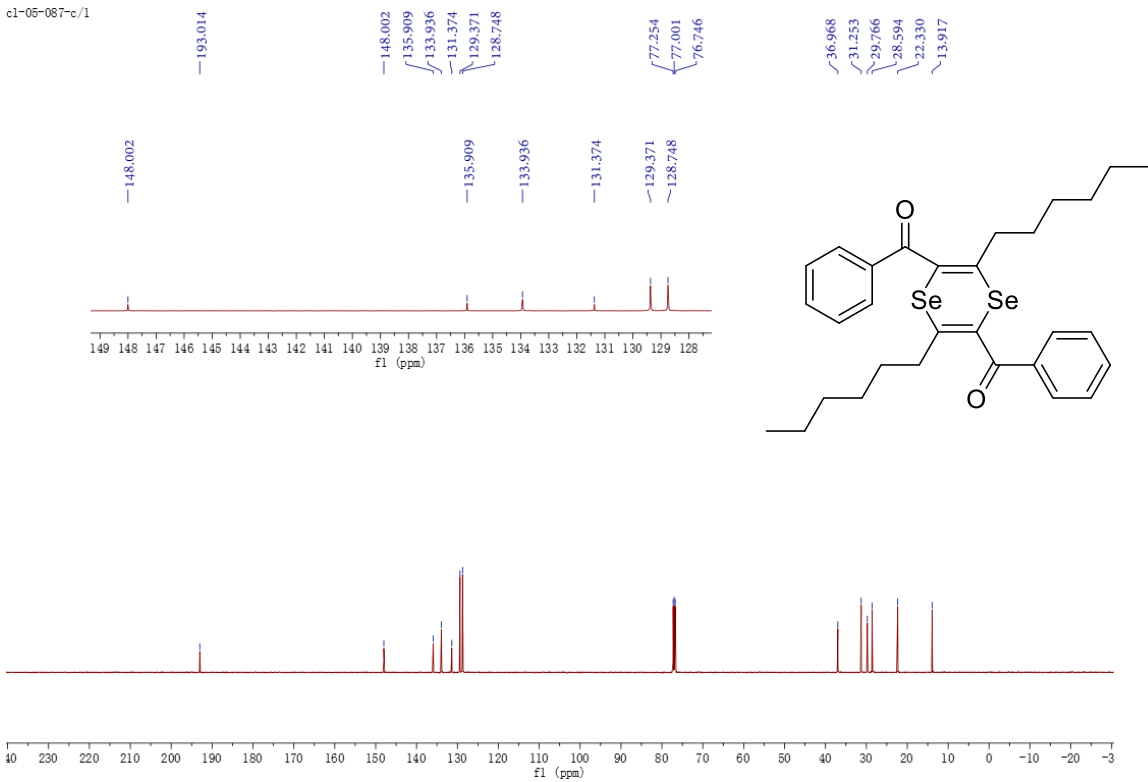
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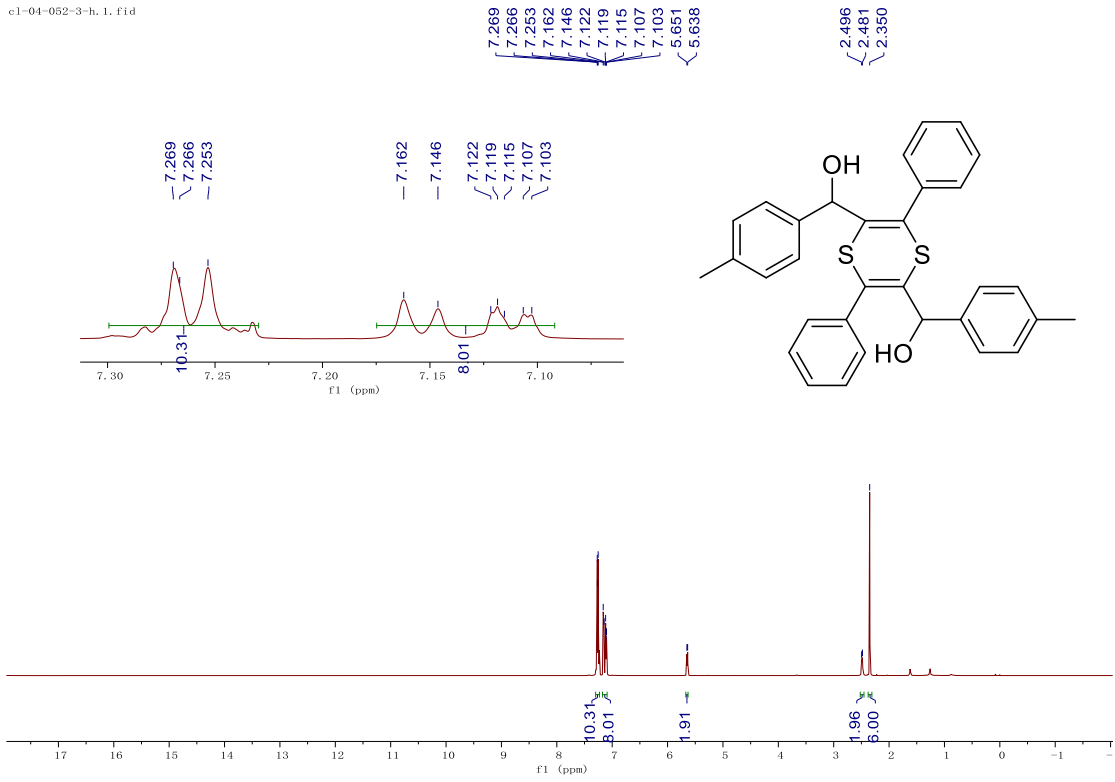
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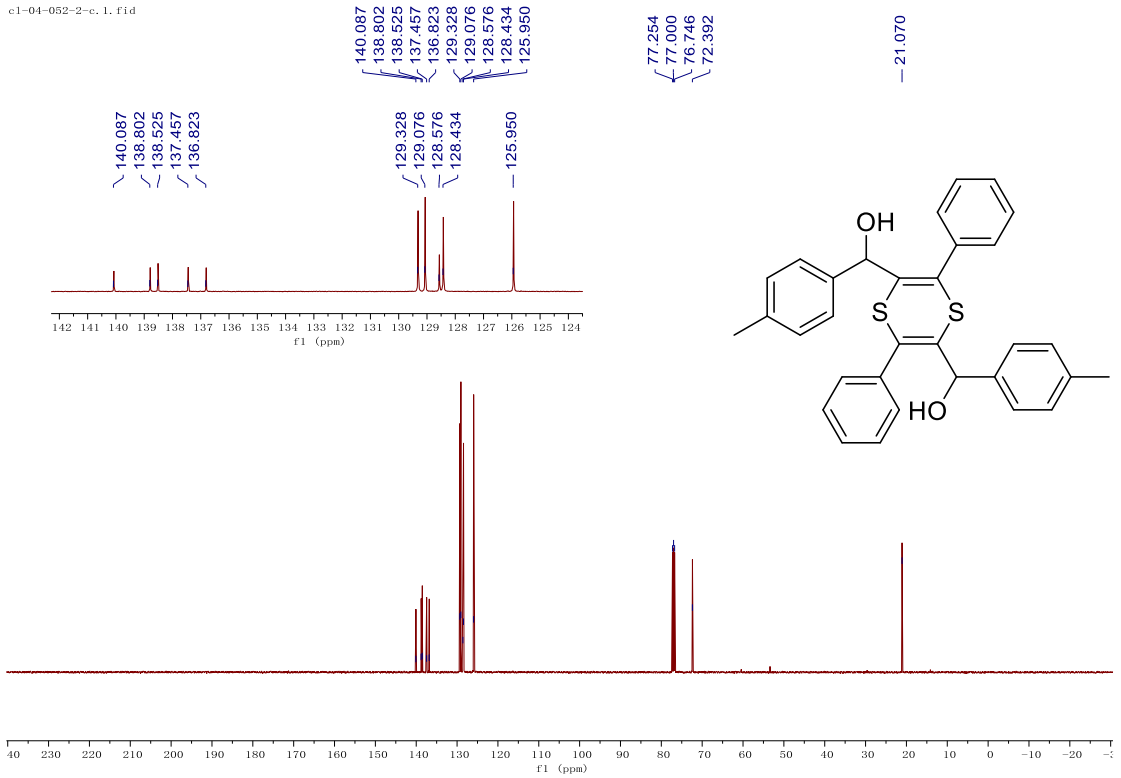
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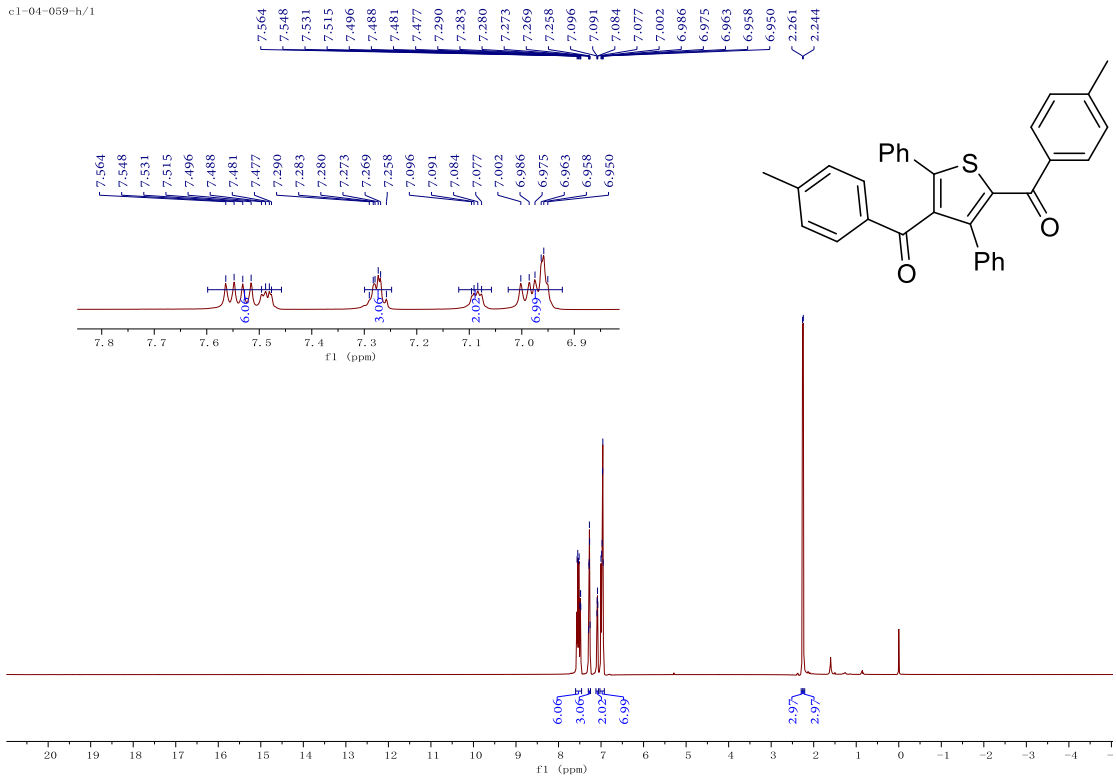
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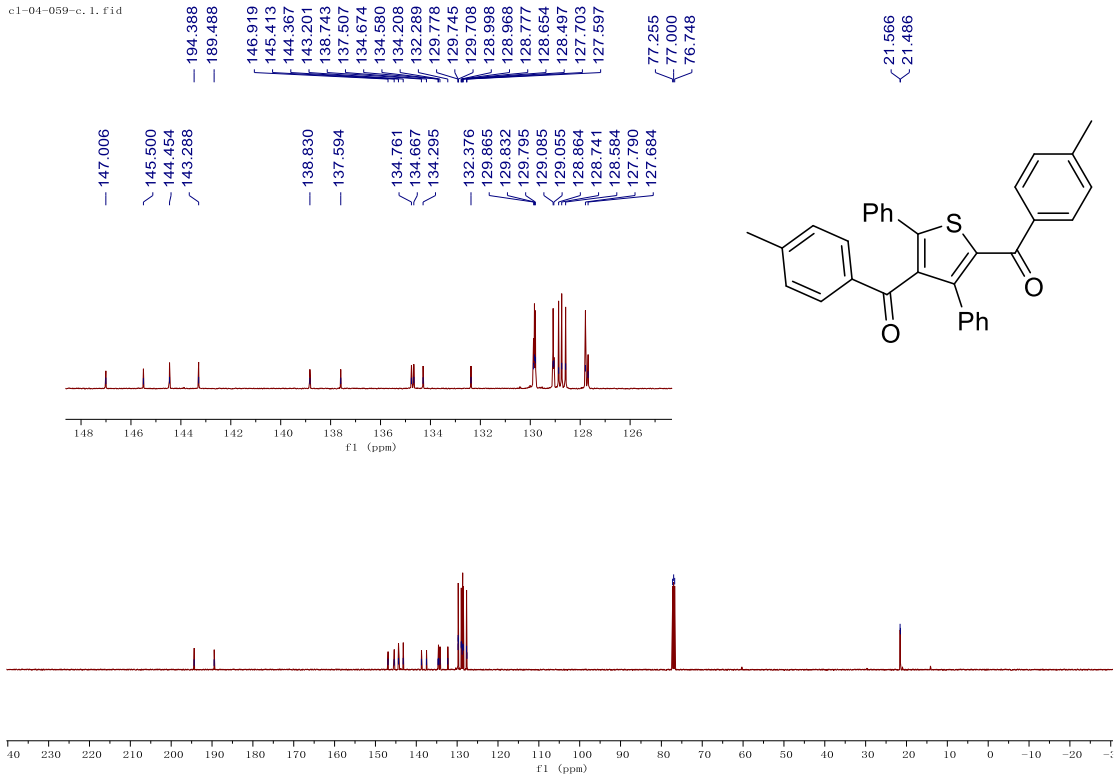
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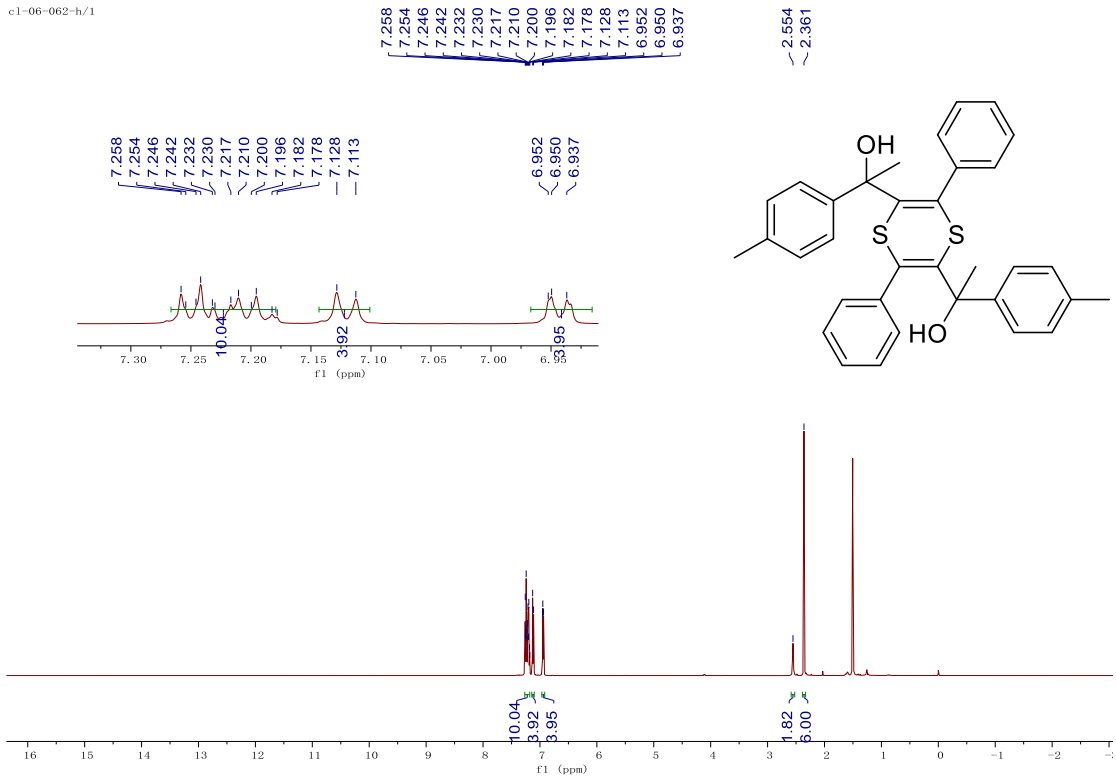
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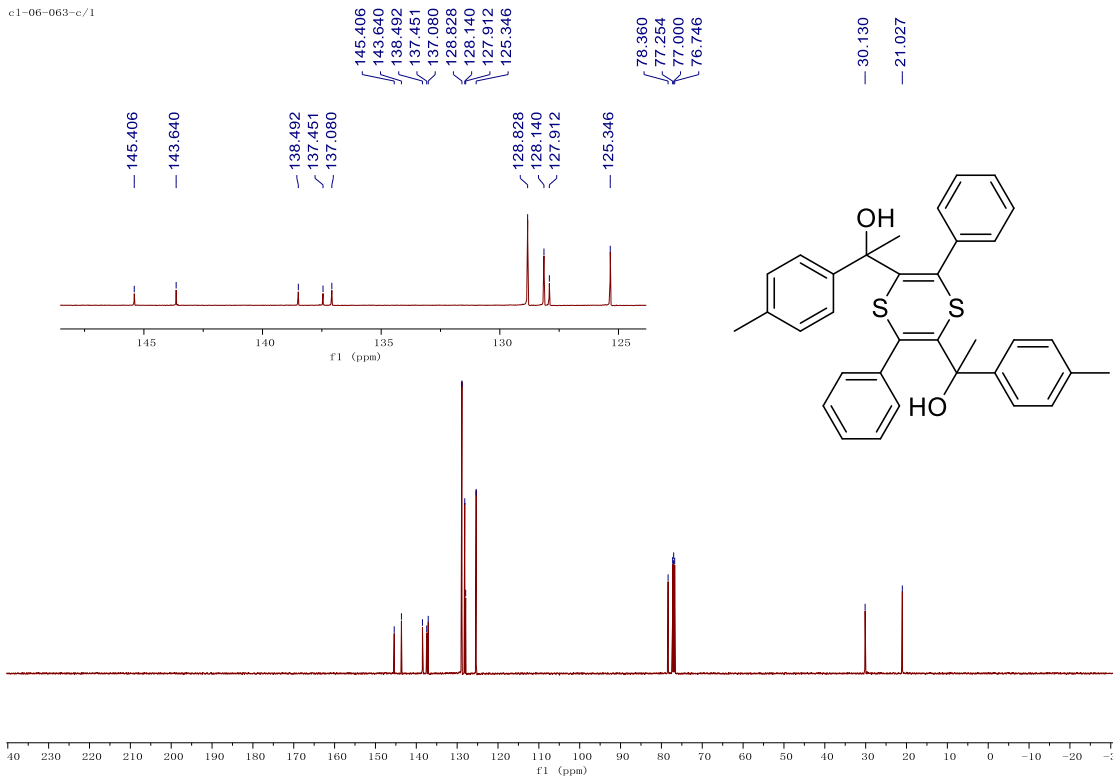
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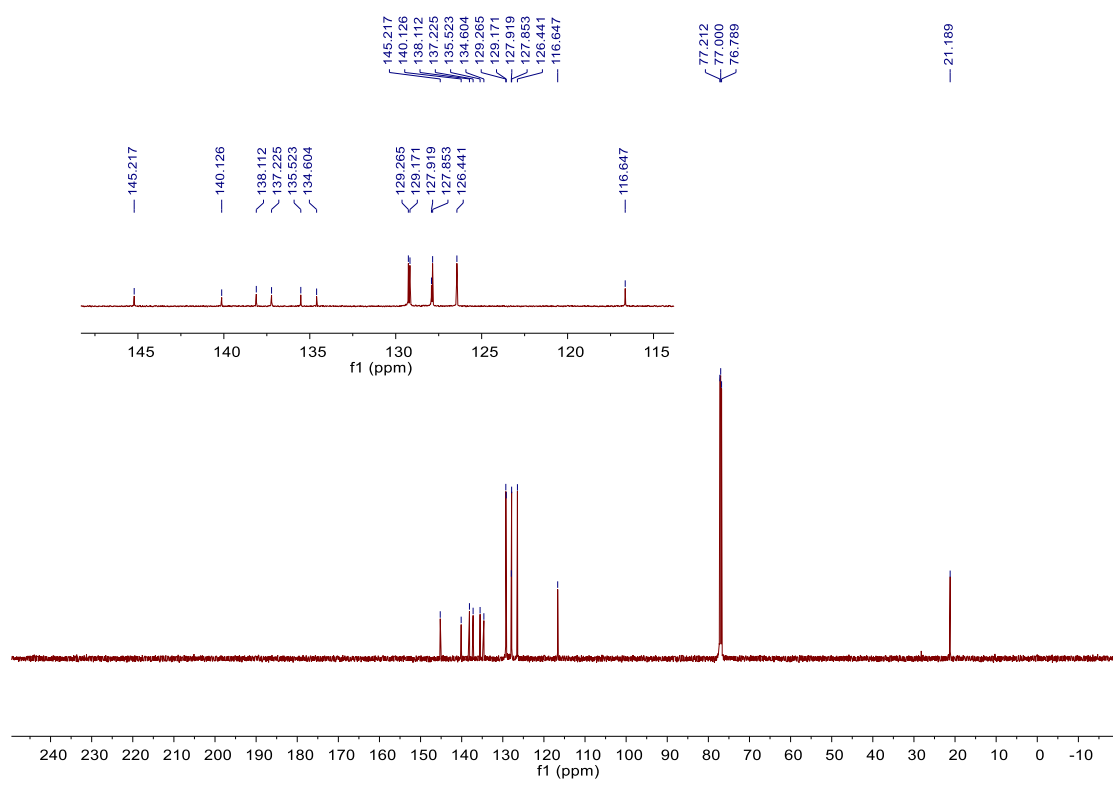
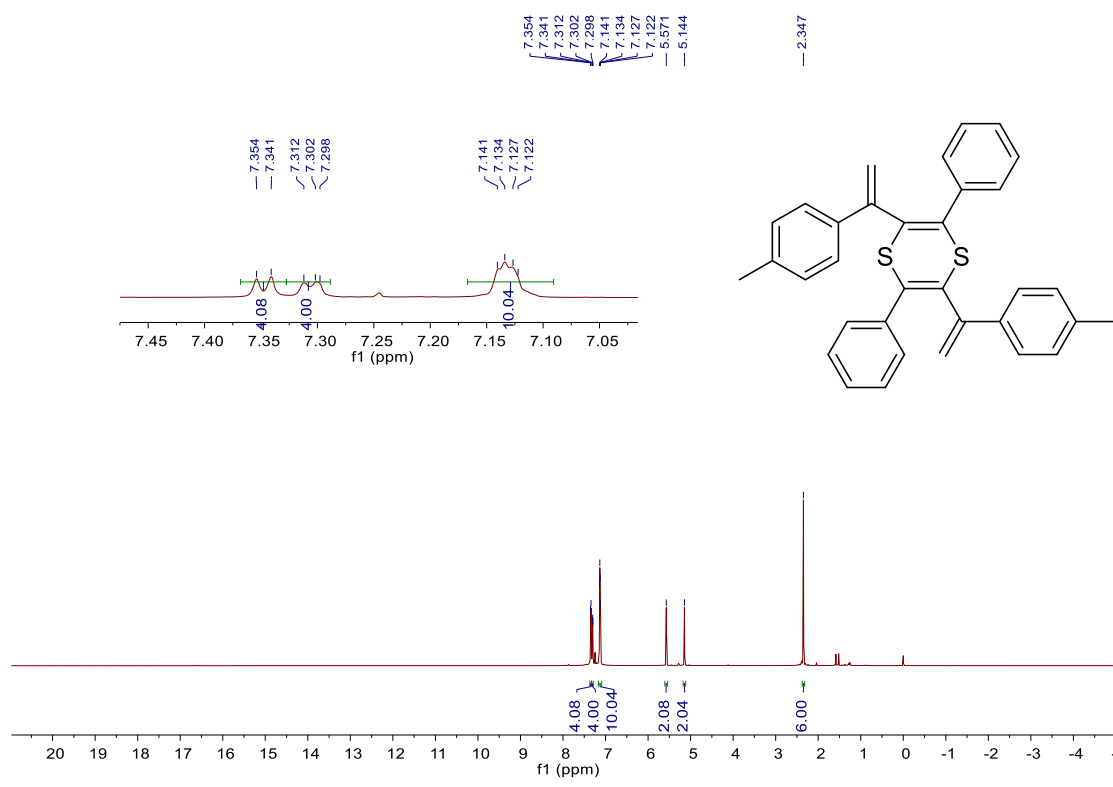


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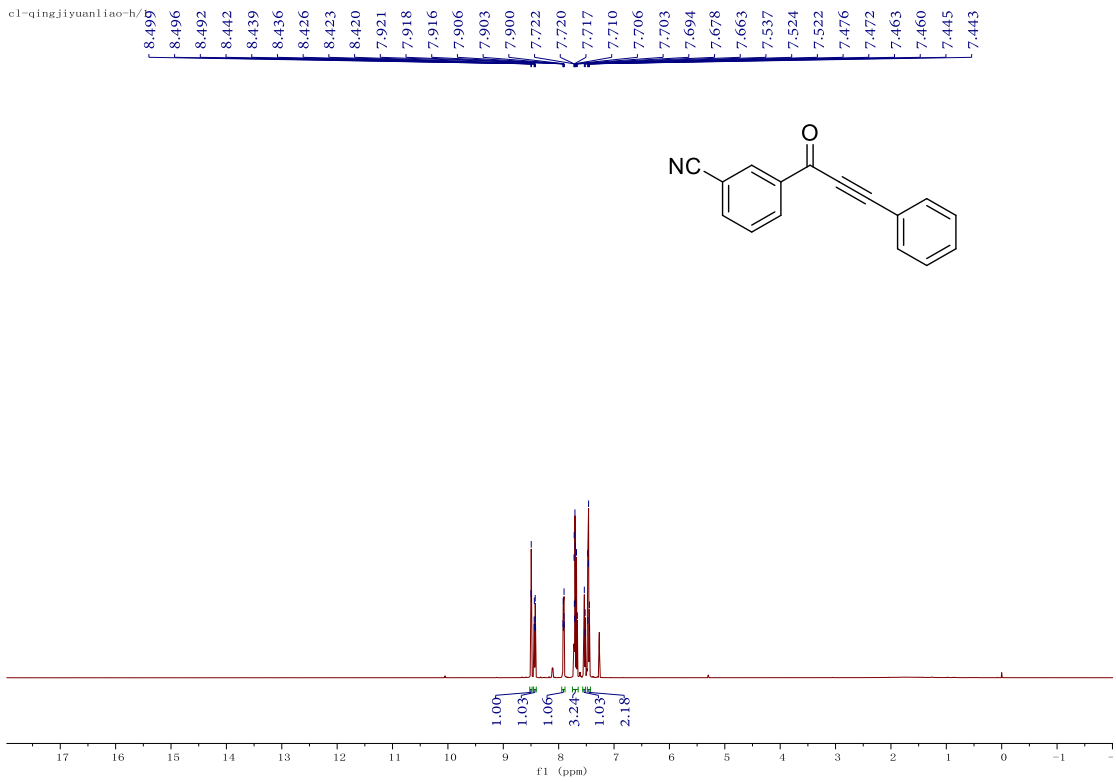


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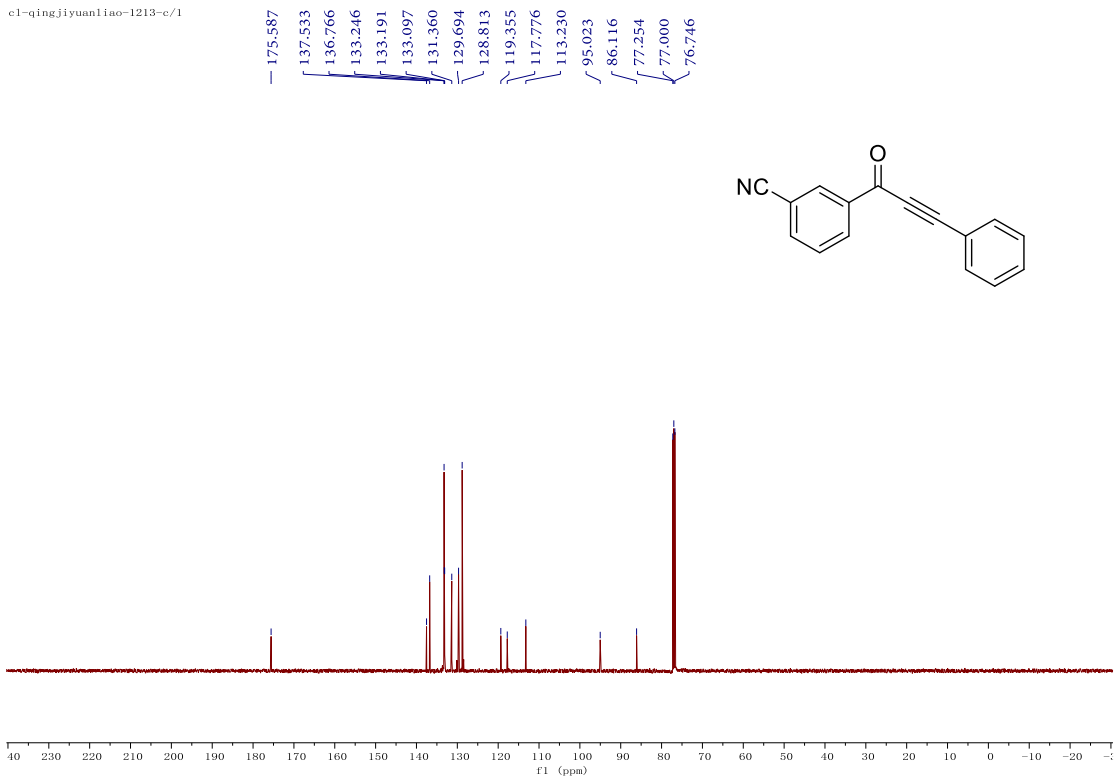




cl-qingjiyuanliao-h/



cl-qingjiyuanliao-1213-c/1



6. X-Ray Crystal Structure of 3h (CCDC: 2201657)

(3,6-diphenyl-1,4-dithiine-2,5-diyl)bis((1-methyl-1H-indol-2-yl)methanone) (3h)

Sample preparation for crystal growth: Compound **3h** (50 mg) was dissolved in the mixed solvent of dichloromethane/petroleum ether = 3 ml/6 ml in a 50 mL round-bottom flask. The yellow single crystal of **3h** was obtained by slowly evaporating mixed solvent at room temperature under air.

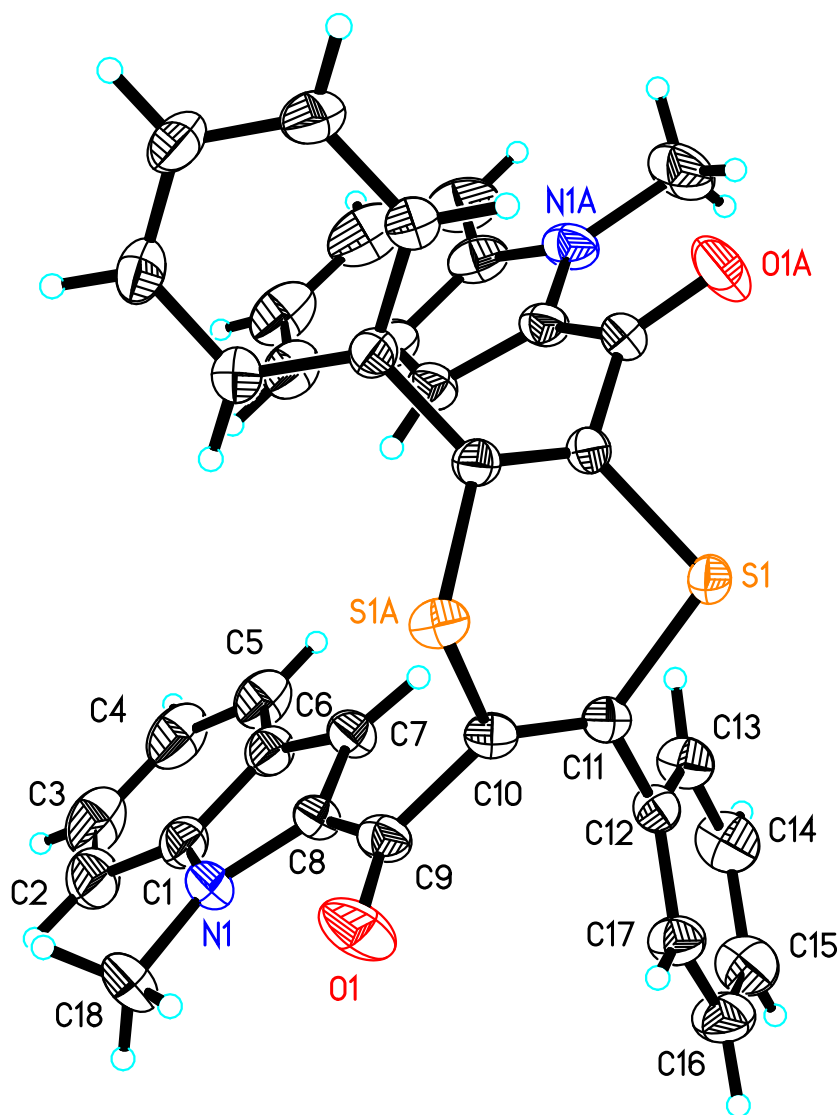


Table S1. Crystal data and structure refinement for **3h**

Identification code	3h
Empirical formula	C ₃₆ H ₂₆ N ₂ O ₂ S ₂
Formula weight	582.71
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 21/c
Unit cell dimensions	a = 16.5229(12) Å α = 90°. b = 10.3183(8) Å β = 114.004(2)°. c = 19.3418(16) Å γ = 90°.
Volume	3012.4(4) Å ³
Z	4
Density (calculated)	1.285 Mg/m ³
Absorption coefficient	0.212 mm ⁻¹
F(000)	1216
Crystal size	0.200 x 0.150 x 0.120 mm ³
Theta range for data collection	2.391 to 25.999°.
Index ranges	-20 ≤ h ≤ 20, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	21487
Independent reflections	2917 [R(int) = 0.0287]
Completeness to theta = 25.242°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6806
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2917 / 0 / 192
Goodness-of-fit on F ²	1.024
Final R indices [I > 2σ(I)]	R1 = 0.0362, wR2 = 0.0961
R indices (all data)	R1 = 0.0403, wR2 = 0.0995
Extinction coefficient	0.0056(18)
Largest diff. peak and hole	0.201 and -0.214 e.Å ⁻³