Supporting Information

H_2O-Controlled Selective Thiocyanation and Alkenylation of Ketene Dithioacetals under Electrochemical Oxidation

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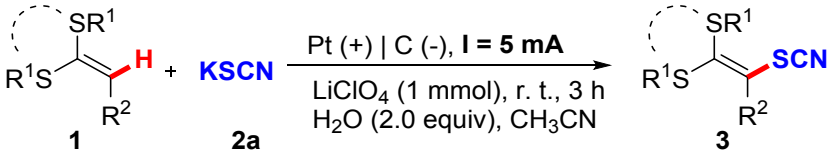
1. General information

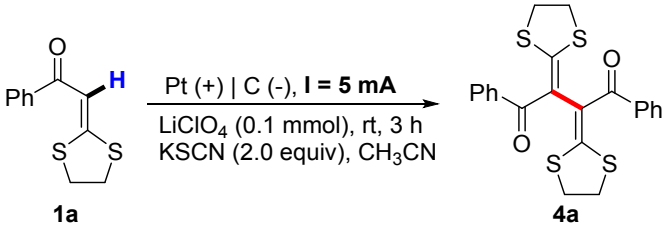
All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Ketene dithioacetalswas prepared according to reported procedures.[1] All the reaction prepared using a high purity deionized (DI) water with a resistivity of 18.0 MΩ•cm from a Barnstead water purification system and the solvent of CH_3CN (99.9%, Extra Dry with molecular sieves, Water≤50 ppm) was purchased from Innochem. The deoxygenation of dideionized water and CH_3CN is through Schlenk technology. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). ^1H and ^{13}C NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

2. General procedure for thiocyanation of ketene dithioacetals under electrochemical oxidation.



In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, ketene dithioacetal **1** (0.25 mmol), potassium thiocyanate **2a** (0.5 mmol, 48.5 mg) and lithium perchlorate (1 mmol, 106 mg) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm^2) anode and graphite rod cathode and was then charged with nitrogen. Under the protection by nitrogen, H_2O (0.5 mmol, 9 μL) and CH_3CN (10 mL) were slowly injected into the reaction tube. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA cm^{-2} under room temperature for 3 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1 - 10:1).

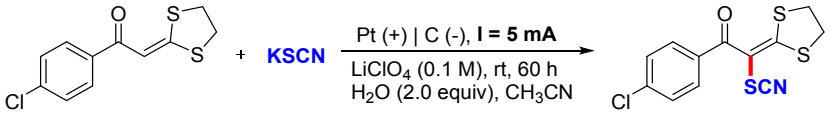
3. Table S1. Optimization of the alkenylation reaction conditions



entry	deviation from standard conditions	Yield [b] (%)
1	none	81
2	without current	n. d.
3	without KSCN	n. d.
4	2 equiv of H_2O	n. d.
5	$^nBu_4NBF_4$ instead of $LiClO_4$	65
6	$^nBu_4NClO_4$ instead of $LiClO_4$	trace
7	$^nBu_4NPF_6$ instead of $LiClO_4$	26
8	KSCN (10 mol%) instead of KSCN (2 equiv)	24
9	KOAc instead of KSCN	trace

[a] Reaction conditions: **1** (0.25 mmol, 55.5 mg), KSCN (0.5 mmol, 48.5 mg), $LiClO_4$ (0.1 M, 106 mg), CH_3CN (10 mL), r. t., N_2, 3 h. [b] Isolated yields.

4. Procedure for gram scale synthesis.

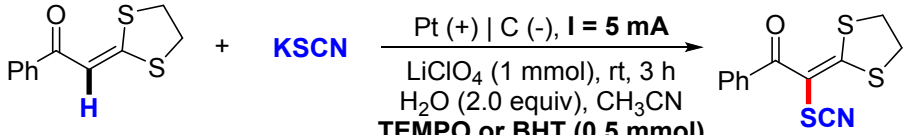


1f (5 mmol) **3fa,** 80%, 1.252 g

In an oven-dried undivided three-necked bottle (250 mL) equipped with a stir bar, 1-(4-chlorophenyl)-2-(1, 3-dithiolan-2-ylidene)ethan-1-one **1f** (5 mmol), potassium thiocyanate **2a** (10 mmol) and lithium perchlorate (20 mmol) were combined and added. The bottle was equipped with platinum plate (1 × 1 cm^2) anode and graphite rod cathode and was then charged with nitrogen. Under the protection by nitrogen, H_2O (10 mmol) and CH_3CN (200 mL) were slowly injected into the reaction tube. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA cm^{-2} under room temperature for 60 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (100 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained in 80% yield by flash column chromatography on silica gel (petroleum: ethyl ether = 5:1).

5. **Preliminary mechanistic studies.**

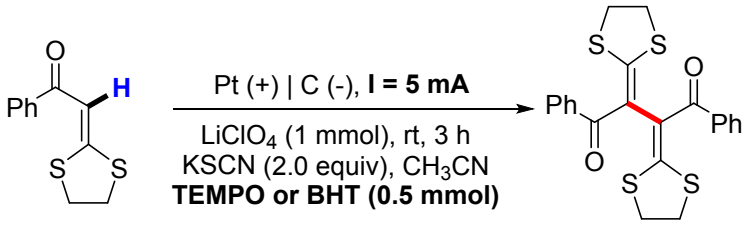
(1) The reaction of **1a** and **2a** with TEMPO or BHT under the standard conditions.



1a **2a** Yield of **3aa**
TEMPO: 19%
BHT: trace

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, ketene dithioacetals **1a** (0.25 mmol), **2a** (0.5 mmol), $LiClO_4$ (1 mmol), H_2O (0.5 mmol), TEMPO or BHT (0.5 mmol) and CH_3CN (10 mL) were combined and sealed. The bottle was equipped with platinum electrodes (1 × 1 cm^2) as anode and graphite rod as cathode, and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction was finished, the solution was concentrated in vacuum and the yield of **3aa** was sharply decreased.

(2) The alkenylation reaction with TEMPO or BHT under the standard conditions.

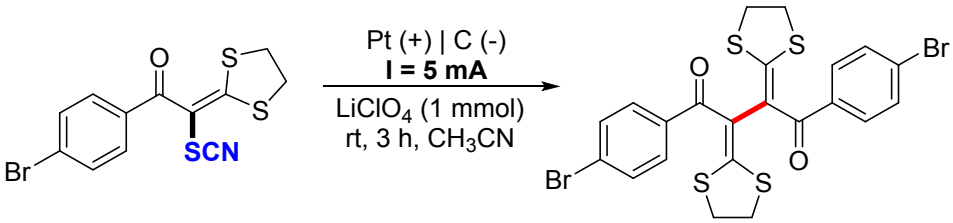


1a

Yield of **4a**
TEMPO: 74%
BHT: 65%

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, **1a** (0.25 mmol), $LiClO_4$ (1 mmol), KSCN (0.5 mmol), TEMPO or BHT (0.5 mmol) and CH_3CN (10 mL) were combined and sealed. The bottle was equipped with platinum electrodes (1 × 1 cm^2) as anode and graphite rod as cathode, and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained in 74% and 65% yield by flash column chromatography on silica gel (petroleum: ethyl ether = 2:1).

(3) The reaction of **3ga** under the alkenylation conditions.



3ga

4d: 23%

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, **3ga** (0.25 mmol), $LiClO_4$ (1 mmol) and CH_3CN (10 mL) were combined and sealed. The bottle was equipped with platinum electrodes (1 × 1 cm^2) as anode and graphite rod as cathode, and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction was finished, the home-coupling product **4d** was obtained in 23% isolatded yield by flash column chromatography on silica gel (petroleum: ethyl ether = 2:1).

(4) Cyclic Voltammetry of **1a** and KSCN.

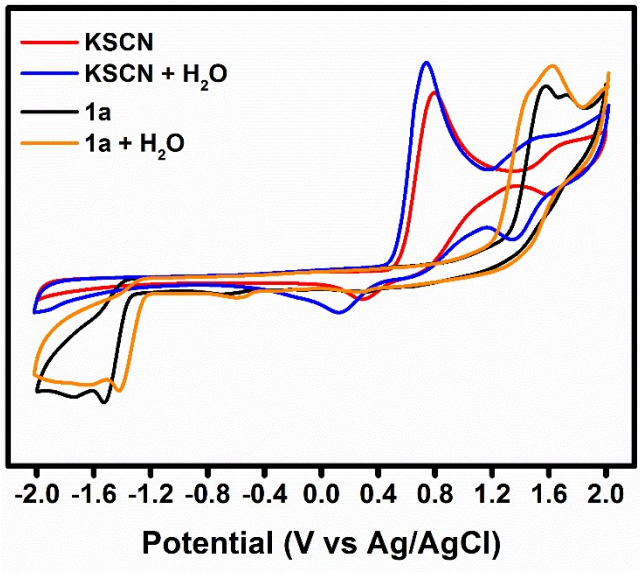


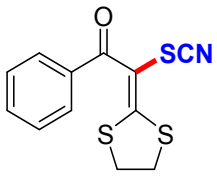
Figure S1. Cyclic Voltammetry of **1a** and KSCN. Glass carbon as working electrode, Pt wire as counter electrode, Ag/AgCl as reference, $LiClO_4$ (0.1M) as electrolyte in CH_3CN, scan rate: 50 mV/s.

6. References

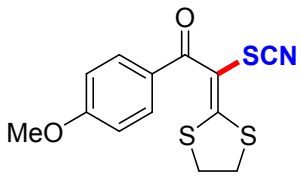
1. (a) L. Zhu, H. Yu, Q. Guo, Q. Chen, Z. Xu, *Org. Lett.* 2015, **17**, 1978; (b) C. Xu, J. Liu, W. Ming; Y. Liu, J. Liu, M. Wang, Q. Liu, *Chem. Eur.* 2013, **19**, 9104; (c) Y. Yin, Q. Zhang, Q. Liu, Y. Liu, S. Sun, *Synth. Commun.* 2007, **37**, 703; (d) W. Tobias, P. Joachim, *Synlett.* 2006, **13**, 2043; (e) T. Okuyama, W. Fujiwara, T. Fueno, *Bull. Chem. Soc. Jpn.* 1986, **59**, 453; (f) W. Jin, W. Du, Q. Yang, H. Yu, Chen, J.; Yu, Z.,*Org. Lett.* 2011, **13**, 4272.

2. Q. Chen, Y. Lei, Y. Wang, C. Wang, Y. Wang, Z. Xu, H.Wang, R. Wang, *Org. Chem. Front.* 2017, **4**, 369.

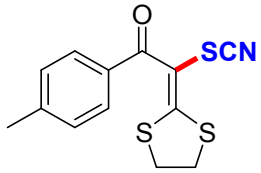
7. Detail descriptions for products.



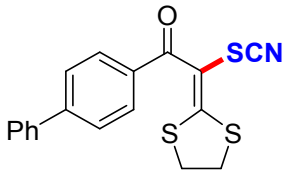
2-(1,3-dithiolan-2-ylidene)-1-phenyl-2-thiocyanatoethan-1-one (3aa):[2] yellow solid was obtained with 96% isolated yield (67.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.50 – 7.42 (m, 1H), 7.39 (t, J = 7.4 Hz, 2H), 3.61 (t, J = 6.05 Hz, 2H), 3.49 (t, J = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.99, 185.98, 137.98, 131.48, 128.22, 128.15, 109.70, 100.96, 41.42, 36.58. HRMS (EI) calcd for $C_{12}H_9NONaS_3$ $[M+Na]^+$: 307-9738; found: 307.9838.



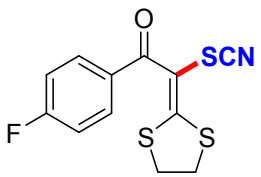
2-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)-2-thiocyanatoethan-1-one (3ba):[2] yellow solid was obtained with 96% isolated yield (74.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 183.94, 179.58, 157.80, 126.19, 125.26, 108.76, 105.02, 96.14, 50.74, 36.47, 31.87. HRMS (EI) calcd for $C_{13}H_{11}NO_2NaS_3$ $[M+Na]^+$: 331.9844; found:331.9842.



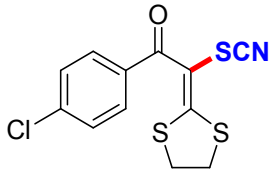
2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(p-tolyl)ethan-1-one (3ca):[2] yellow solid was obtained with 98% isolated yield (66.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 6.5 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.49 (t, *J* = 6.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 185.01, 180.39, 137.50, 130.30, 124.13, 123.73, 104.97, 96.30, 36.56, 31.82, 16.91. HRMS (EI) calcd for $C_{13}H_{11}NONaS_3$ $[M+Na]^+$: 315.9895; found: 315.9896.



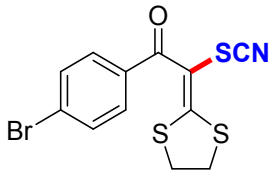
1-([1,1'-biphenyl]-4-yl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3da):[2] yellow oil was obtained with 88% isolated yield (78.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 3.70 (t, *J* = 6.6 Hz, 2H), 3.58 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.55, 185.85, 144.37, 140.03, 136.59, 128.94, 128.08, 127.28, 126.87, 109.72, 100.99, 41.38, 36.58. HRMS (EI) calcd for $C_{18}H_{13}NNaONaS_3$ $[M+Na]^+$: 378.0051; found: 378.0047.



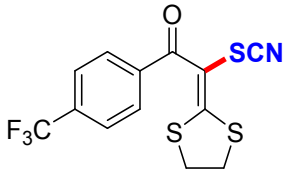
2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)-2-thiocyanatoethan-1-one (3ea):[2] yellow solid was obtained with 96% isolated yield (71.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.63 (m, 2H), 7.19 – 7.06 (m, 2H), 3.71 (t, *J* = 6.6 Hz, 2H), 3.59 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.58, 186.42, 164.60 (d, *J* = 252.9 Hz), 134.03, 130.83 (d, *J* = 8.9 Hz), 115.40 (d, *J* = 22.0 Hz), 109.58, 100.63, 41.43, 36.62. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.09. HRMS (EI) calcd for $C_{12}H_8FNNaOS_3$ $[M+Na]^+$: 319.9644; found: 319.9641.



1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3fa):[2] yellow solid was obtained with 97% isolated yield (76.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 3.72 (t, *J* = 6.6 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.74, 186.85, 137.74, 136.29, 129.67, 128.54, 109.52, 100.60, 41.47, 36.59. HRMS (EI) calcd for $C_{12}H_8ClNONaS_3$ $[M+Na]^+$: 335.9349; found: 335.9344.

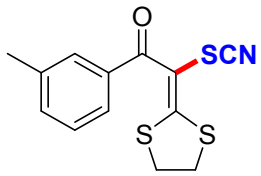


1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3ga):[2] yellow solid was obtained with 94% isolated yield (83.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.50 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.83 (s), 186.99, 136.78, 131.50, 129.77, 126.19, 109.54, 100.55, 41.50, 36.61. HRMS (EI) calcd for $C_{12}H_8BrNONaS_3$ $[M+Na]^+$: 379.8844; found: 379.8845.

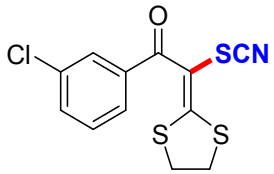


2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ha):[2] yellow solid was obtained with 88% isolated yield (75.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 4H), 3.70 – 3.63 (t, *J* = 6.2 Hz, 2H), 3.52 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 184.10 (s), 183.29 (s), 136.75 (s), 128.04 (q, *J* = 33.28 Hz), 124.91, 123.46, 121.18(q, *J* = 273.3 Hz), 120.55 (q, *J* =

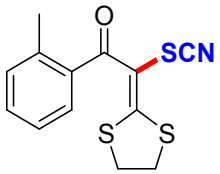
3.6 Hz), 104.67, 95.74, 36.88, 31.84. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.93. HRMS (EI) calcd for $C_{13}H_8F_3NONaS_3$ $[M+Na]^+$: 369.9612; found: 369.9609.



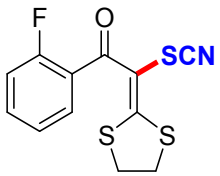
2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(m-tolyl)ethan-1-one (3ia):[2] yellow solid was obtained with 83% isolated yield (61.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 2H), 3.60 (t, *J* = 6.1 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.25, 185.59, 138.12, 137.95, 132.28, 128.70, 128.05, 125.22, 109.75, 101.07, 41.38, 36.58, 21.39. HRMS (EI) calcd for $C_{13}H_{11}NONaS_3$ $[M+Na]^+$:315.9895; found: 315.9893.



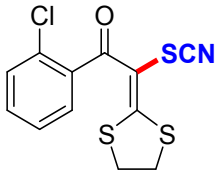
1-(3-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3ja):[2] yellow solid was obtained with 84% isolated yield (65.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 3.64 (t, *J* = 6.7 Hz, 2H), 3.51 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.48, 187.30, 139.69, 134.43, 131.38, 129.54, 128.17, 126.07, 109.43, 100.56, 41.52, 36.61. HRMS (EI) calcd for $C_{12}H_8ClNONaS_3$ $[M+Na]^+$: 335.9349; found: 335.9344.



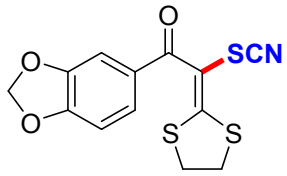
2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(o-tolyl)ethan-1-one (3ka):[2] yellow solid was obtained with 85% isolated yield (62.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 1H), 7.21 – 7.12 (m, 3H), 3.66 – 3.59 (t, *J* = 6.2 Hz, 1H), 3.51 – 3.46 (t, *J* = 7.2 Hz, 1H), 2.23 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.05, 185.63, 138.71, 135.06, 130.74, 129.81, 126.22, 125.50, 109.51, 102.34, 41.68, 36.52, 19.37. HRMS (EI) calcd for $C_{13}H_{11}NOS_3Na$ $[M+Na]^+$: 315.9895; found: 315.9893.



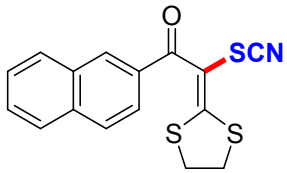
2-(1,3-dithiolan-2-ylidene)-1-(2-fluorophenyl)-2-thiocyanatoethan-1-one (3la):[2] yellow solid was obtained with 84% isolated yield (62.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.31 (m, 2H), 7.19 (dd, *J* = 10.0, 4.9 Hz, 1H), 7.05 (t, *J* = 9.0 Hz, 1H), 3.63 (t, *J* = 6.7 Hz, 2H), 3.49 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.70, 186.35, 158.78 (d, *J* = 248.3 Hz), 132.71 (d, *J* = 8.3 Hz), 129.54 (d, *J* = 3.1 Hz), 127.12 (d, *J* = 16.0 Hz), 124.69 (d, *J* = 3.4 Hz), 115.75 (d, *J* = 21.6 Hz), 109.55, 102.35, 41.48, 36.58. ^{19} F NMR (471 MHz, $CDCl_3$) δ -111.82. HRMS (EI) calcd for $C_{12}H_8FNNaOS_3Na$ $[M+Na]^+$: 319.9644; found: 319.9641.



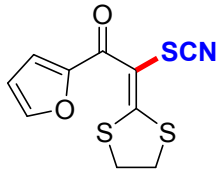
1-(2-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3ma):[2] yellow solid was obtained with 83% isolated yield (65.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 4H), 3.69 – 3.62 (t, *J* = 6.4 Hz, 2H), 3.50 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.65, 186.43, 138.56, 131.01, 130.43, 129.46, 128.07, 127.21, 109.55, 102.16, 41.66, 36.51. HRMS (EI) calcd for $C_{12}H_8ClNONaS_3$ $[M + Na]^+$: 335.9349; found: 335.9344.



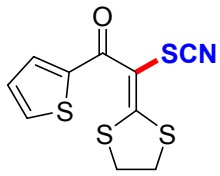
1-(benzo[d][1,3]dioxol-5-yl)-2-(1,3-dithiolan-2-ylidene)-2-thiocyanatoethan-1-one (3na):[2] yellow solid was obtained with 85% isolated yield (68.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 9.7, 1.6 Hz, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.98 (s, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.37, 184.60, 150.76, 147.64, 131.62, 124.35, 109.63, 108.98, 107.86, 101.80, 100.79, 41.25, 36.67. HRMS (EI) calcd for $C_{13}H_9NO_3NaS_3$ $[M+Na]^+$: 345.9637; found: 345.9639.



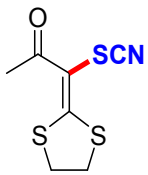
2-(1,3-dithiolan-2-ylidene)-1-(naphthalen-2-yl)-2-thiocyanatoethan-1-one (3oa):[2] yellow solid was obtained with 87% isolated yield (71.7 mg). ^{1}H NMR (500 MHz, DMSO) δ 8.26 (s, 1H), 8.06 – 7.98 (m, 3H), 7.72 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.64 (dtd, *J* = 14.7, 7.0, 1.2 Hz, 2H), 3.78 (t, *J* = 6.5 Hz, 2H), 3.70 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 189.72, 186.08, 136.09, 134.42, 132.30, 129.37, 128.88, 128.44, 128.22, 128.19, 125.09, 111.49, 101.73, 41.91, 37.20. HRMS (EI) calcd for $C_{16}H_{11}NONaS_3$ $[M+Na]^+$: 351.9895; found: 351.9891.



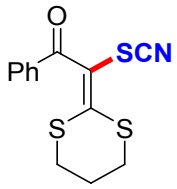
2-(1,3-dithiolan-2-ylidene)-1-(furan-2-yl)-2-thiocyanatoethan-1-one (3pa):[2] yellow sloid was obtained with 95% isolated yield (64.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.0 Hz, 1H), 7.47 (d, *J* = 3.5 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.46 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.28, 169.81, 146.19, 141.92, 115.11, 107.55, 104.97, 93.88, 36.49, 31.35. HRMS (EI) calcd for $C_{10}H_7NO_2NaS_3$ $[M + Na]^+$: 291.9531; found: 291.9527.



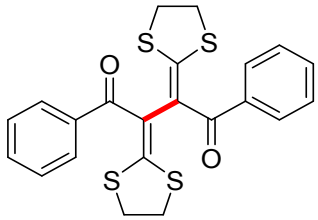
2-(1,3-dithiolan-2-ylidene)-2-thiocyanato-1-(thiophen-2-yl)ethan-1-one (3qa):[2] yellow solid was obtained with 94% isolated yield (67.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 3.9, 1.0 Hz, 1H), 7.60 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.10 (dd, *J* = 4.9, 4.0 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.47 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.27, 178.94, 141.3, 134.27, 133.97, 127.89, 109.41, 99.25, 41.35, 36.18. HRMS (EI) calcd for $C_{10}H_7NNaOS_4$ $[M + Na]^+$: 307.9303; found: 307.9298.



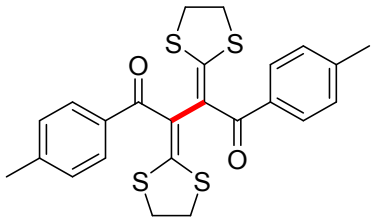
1-(1,3-dithiolan-2-ylidene)-1-thiocyanatopropan-2-one (3ra):[2] yellow solid was obtained with 93% isolated yield (50.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.69 – 3.62 (t, *J* = 6.3 Hz, 2H), 3.53 – 3.48 (t, *J* = 7.1 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.18, 183.68, 109.45, 101.61, 41.66, 36.25, 27.69. HRMS (EI) calcd for $C_7H_7NONaS_3$ $[M + Na]^+$; 239.9582; found: 239.9578.



2-(1,3-dithian-2-ylidene)-1-phenyl-2-thiocyanatoethan-1-one (3sa):[2] white solid was obtained with 82% isolated yield (60.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 2.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.43, 175.14, 137.79, 132.51, 128.99, 128.48, 109.58, 109.54, 30.80, 30.37, 23.83. HRMS (EI) calcd for $C_{13}H_{12}NONaS_3$ $[M + Na]^+$: 315.9895; found: 315.9891.

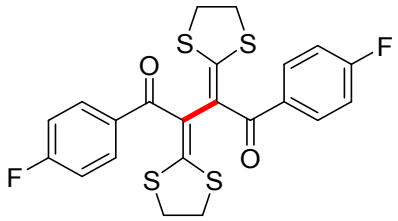


2,3-di(1,3-dithiolan-2-ylidene)-1,4-diphenylbutane-1,4-dione (**4a**): yellow solid was obtained with 81% isolated yield (44.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.50 – 7.42 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 4H), 3.61 (t, *J* = 6.1 Hz, 4H), 3.49 (t, *J* = 6.6 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.98, 185.98, 137.97, 131.48, 128.21, 128.15, 109.70, 41.42, 36.57. HRMS (EI) calcd for $C_{22}H_{19}O_2NaS_4$ $[M + Na]^+$: 465.0082; found: 465.0078.

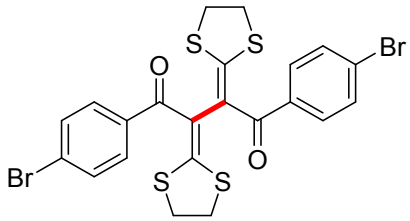


2,3-di(1,3-dithiolan-2-ylidene)-1,4-di-p-tolylbutane-1,4-dione (4b): yellow solid was obtained with 83% isolated yield (48.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 4H), 7.06 (d, *J* = 7.9 Hz, 4H), 3.45 (t, *J* = 6.5 Hz, 4H), 3.35 – 3.29 (t, *J* = 7.0 Hz, 4H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.27, 181.96, 140.82, 136.19, 129.02, 128.08, 114.99, 41.00, 35.65, 21.59. HRMS (EI) calcd

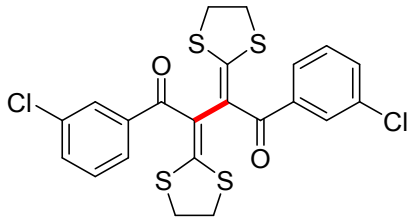
for $C_{24}H_{23}O_2S_4$ $[M+H]^+$: 471.0575; found: 471.0578.



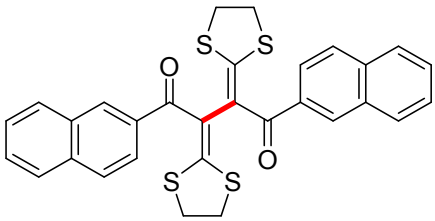
2,3-di(1,3-dithiolan-2-ylidene)-1,4-bis(4-fluorophenyl)butane-1,4-dione (4c): yellow solid was obtained with 78% isolated yield (46.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.5, 5.5 Hz, 4H), 6.95 (t, *J* = 8.7 Hz, 4H), 3.47 (t, *J* = 6.5 Hz, 4H), 3.33 (t, *J* = 6.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.94, 183.27, 164.03 (d, *J* = 251.1 Hz), 134.93, 131.38 (d, *J* = 8.8 Hz), 114.48 (d, *J* = 21.7 Hz), 114.17, 41.05, 35.71. ^{19}F NMR (377 MHz, $CDCl_3$) δ -107.09. HRMS (EI) calcd for $C_{22}H_{17}F_2O_2S_4$ $[M+H]^+$: 479.0074; found: 479.0078.



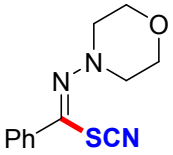
1,4-bis(4-bromophenyl)-2,3-di(1,3-dithiolan-2-ylidene)butane-1,4-dione (4d): yellow solid was obtained with 75% isolated yield (56.1mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 4H), 3.56 (t, *J* = 6.1 Hz, 4H), 3.43 – 3.38 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.13, 184.20, 137.67, 130.67, 130.54, 124.91, 113.74, 41.18, 35.74. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.82. HRMS (EI) calcd for $C_{22}H_{17}Br_2O_2S_4$ $[M+H]^+$: 598.8473; found: 598.8478.



1,4-bis(3-chlorophenyl)-2,3-di(1,3-dithiolan-2-ylidene)butane-1,4-dione (4e): yellow solid was obtained with 70% isolated yield (44.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 1.7 Hz, 2H), 7.33 – 7.28 (m, 4H), 7.23 – 7.18 (m, 2H), 3.49 (t, *J* = 6.1 Hz, 4H), 3.34 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.86, 184.09, 140.63, 133.53, 130.38, 128.80, 126.84, 114.11, 41.17, 35.71. HRMS (EI) calcd for $C_{22}H_{17}Cl_2O_2S_4$ $[M+H]^+$: 510.9483; found: 510.9488.



2,3-di(1,3-dithiolan-2-ylidene)-1,4-di(naphthalen-2-yl)butane-1,4-dione (4f): yellow solid was obtained with 84% isolated yield (57.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.69 (dd, *J* = 16.1, 8.2 Hz, 4H), 7.48 – 7.35 (m, 6H), 3.34 (t, *J* = 6.4 Hz, 4H), 3.21 (t, *J* = 6.4 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.23, 183.16, 136.42, 134.16, 132.21, 129.42, 129.26, 127.61, 127.24, 126.85, 126.13, 125.76, 114.48, 41.01, 35.63. HRMS (EI) calcd for $C_{30}H_{23}O_2S_4$ $[M+H]^+$: 543.0575; found: 543.0578.

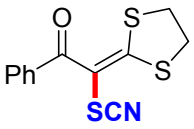


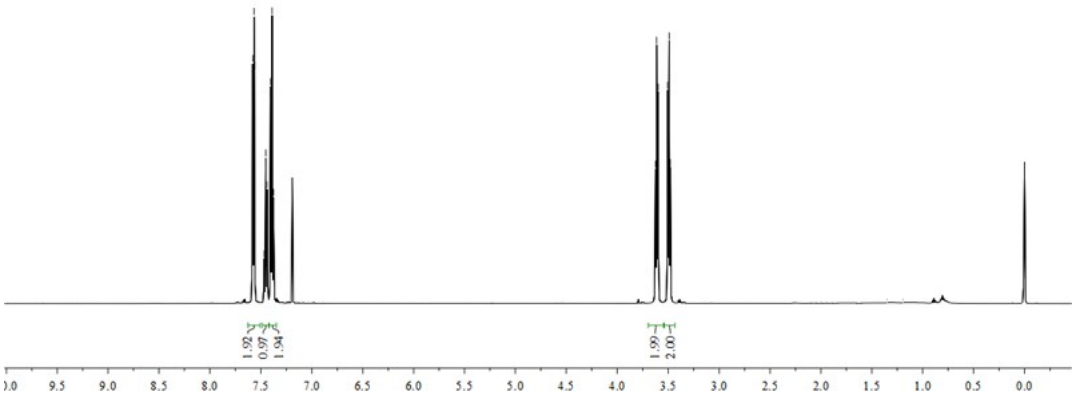
Z)-cyanic (Z)-N-morpholinobenzimidic thioanhydride (5a):[2] yellow solid was obtained with 95% isolated yield (58.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.21 (s, 4H), 3.77 – 2.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.55, 178.02, 133.05, 129.23, 128.74, 127.90, 63.07, 60.16. HRMS (EI) calcd for $C_{12}H_{13}N_3NaOS$ $[M+Na]^+$: 270.0672; found 270.0675.

8. Copies of product NMR Spectra

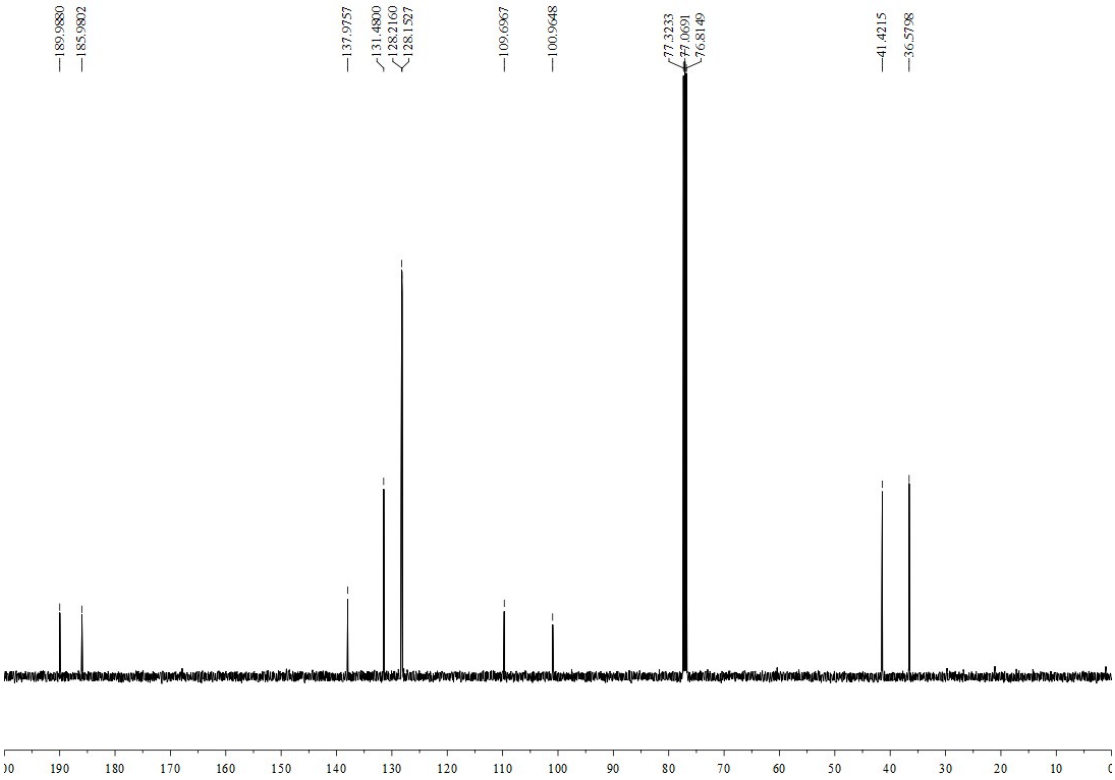
3aa

^{1}HNMR



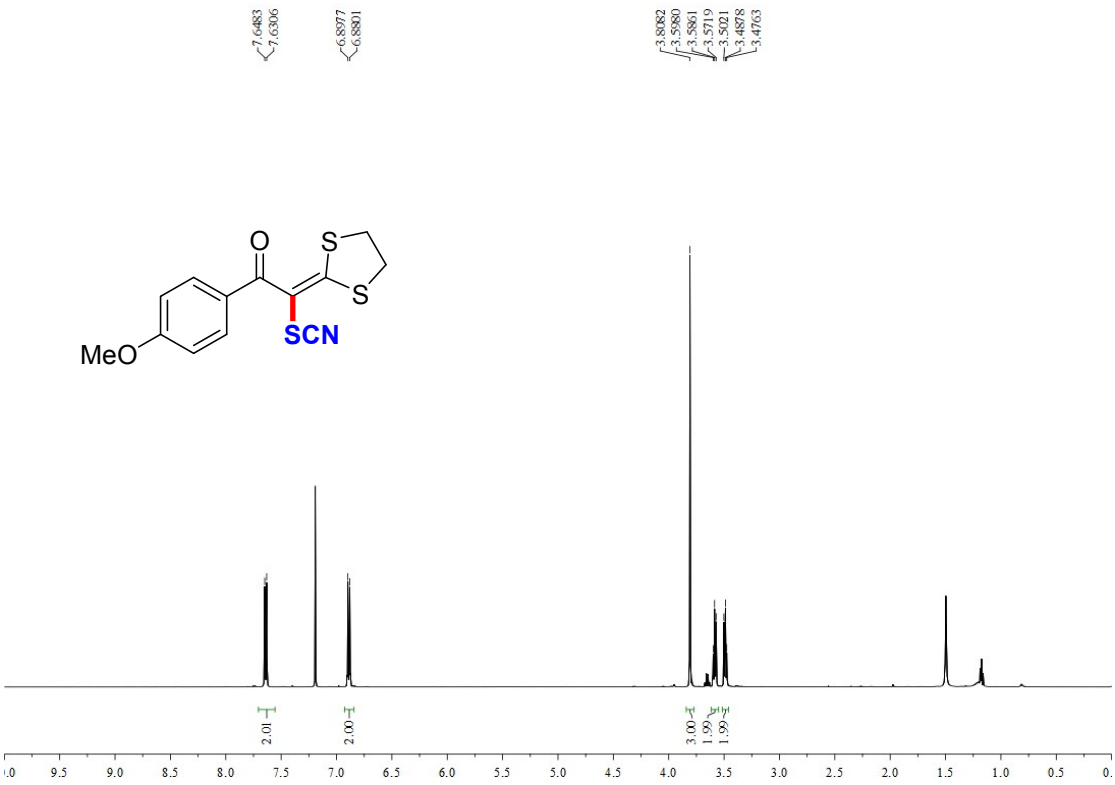


^{13}CNMR



3ba

[1]HNMR



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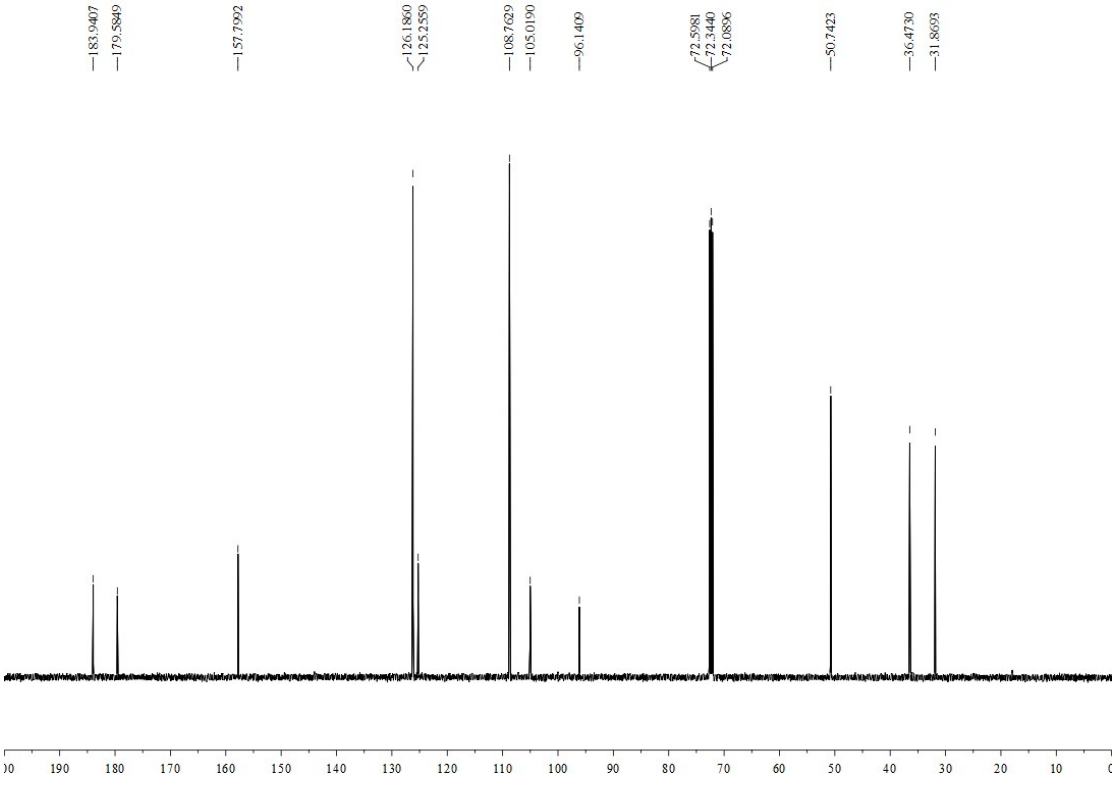
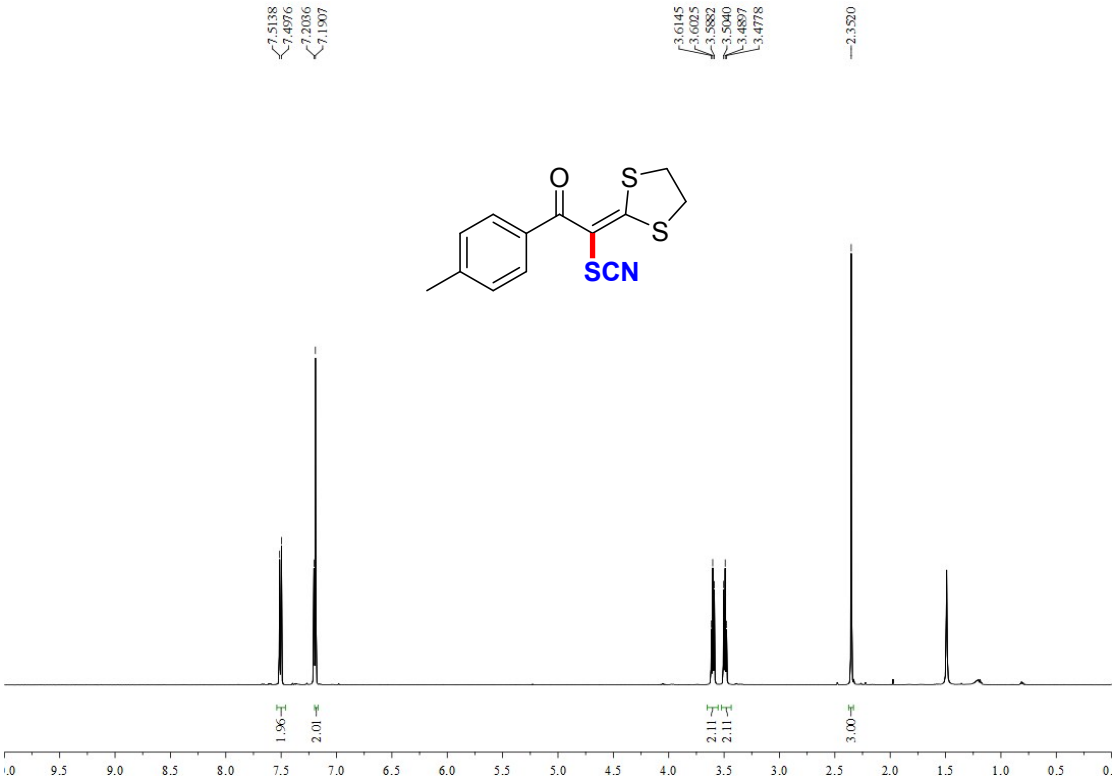
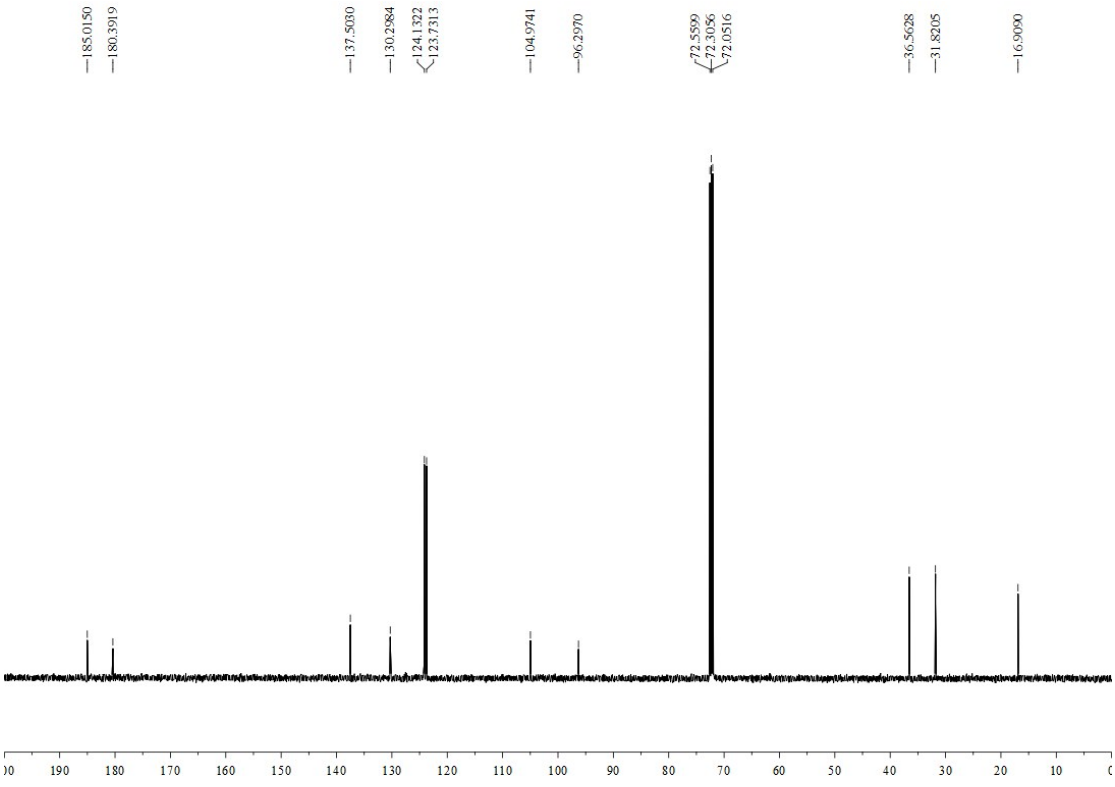


3ca

[1]HNMR

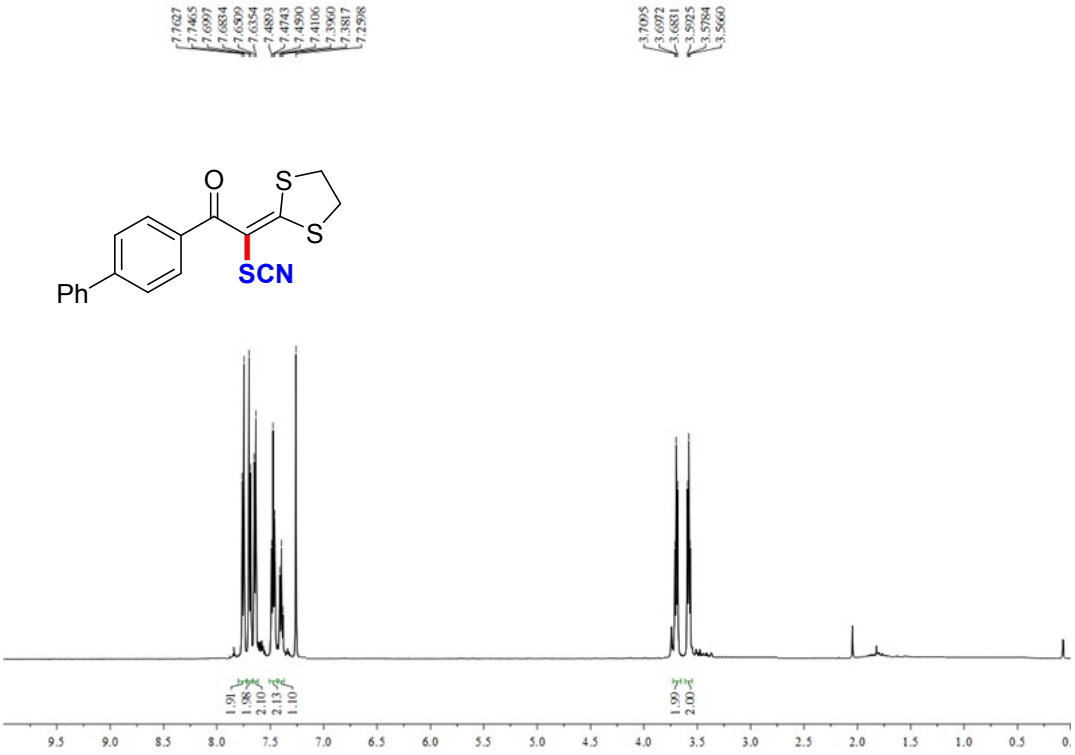


[13]CNMR

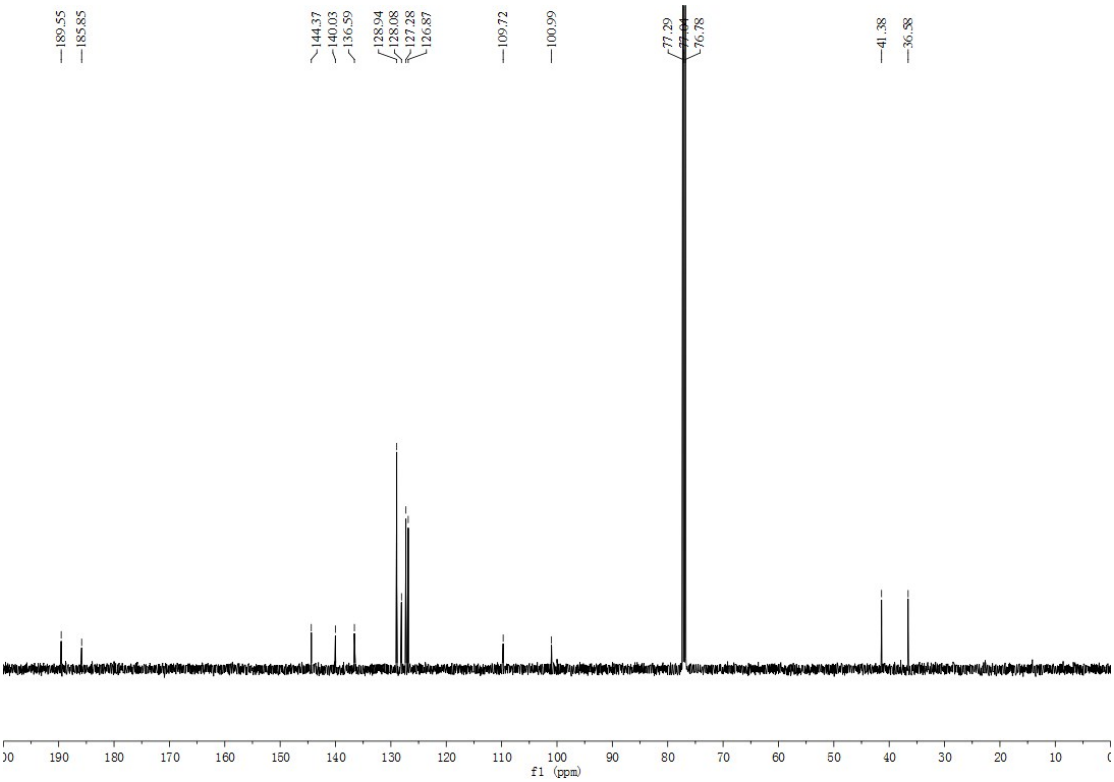


3da

[1]HNMR



[13]CNMR



3ea

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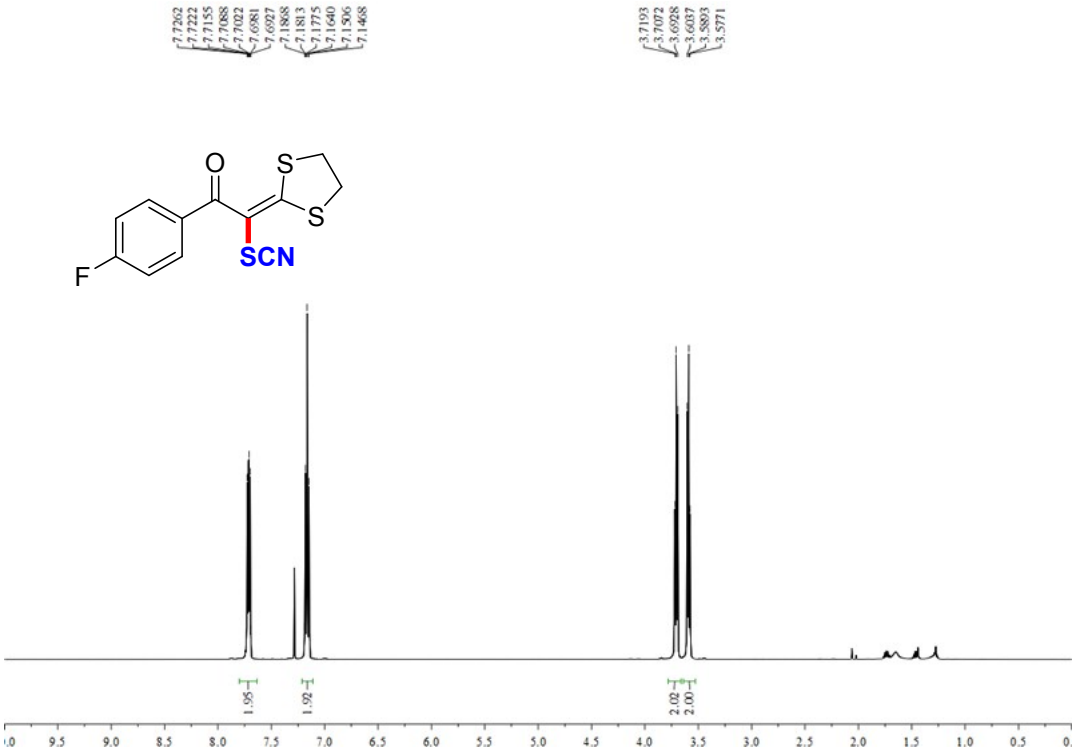

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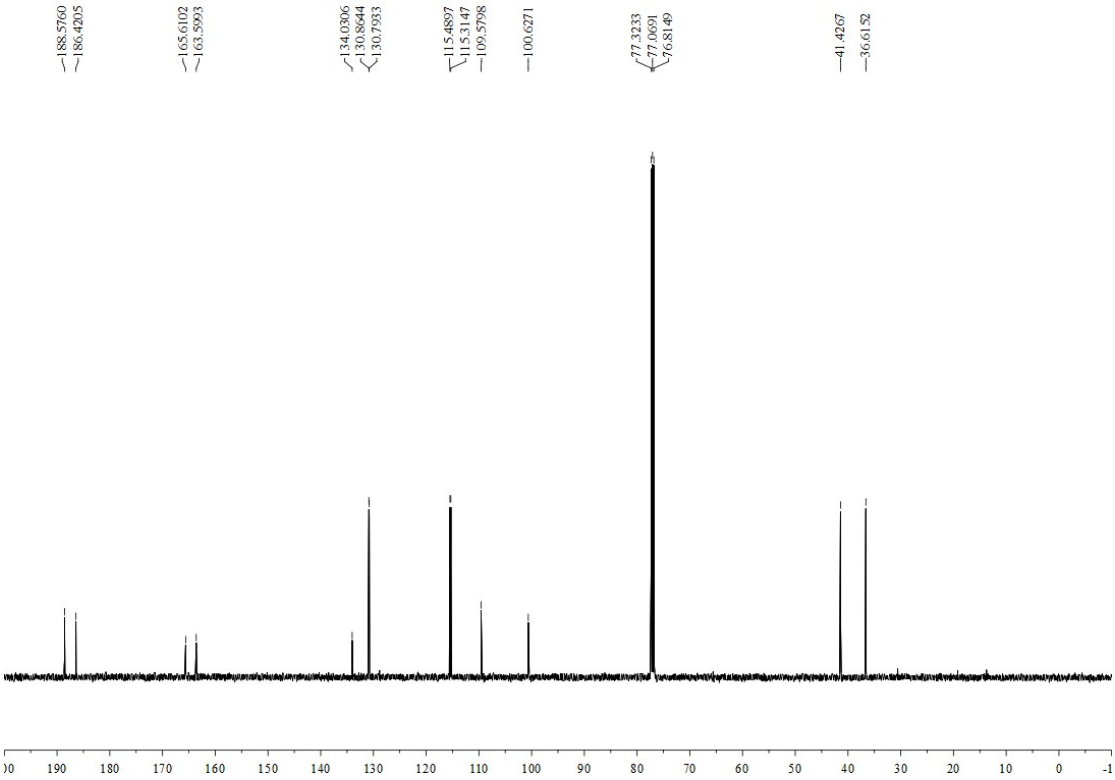

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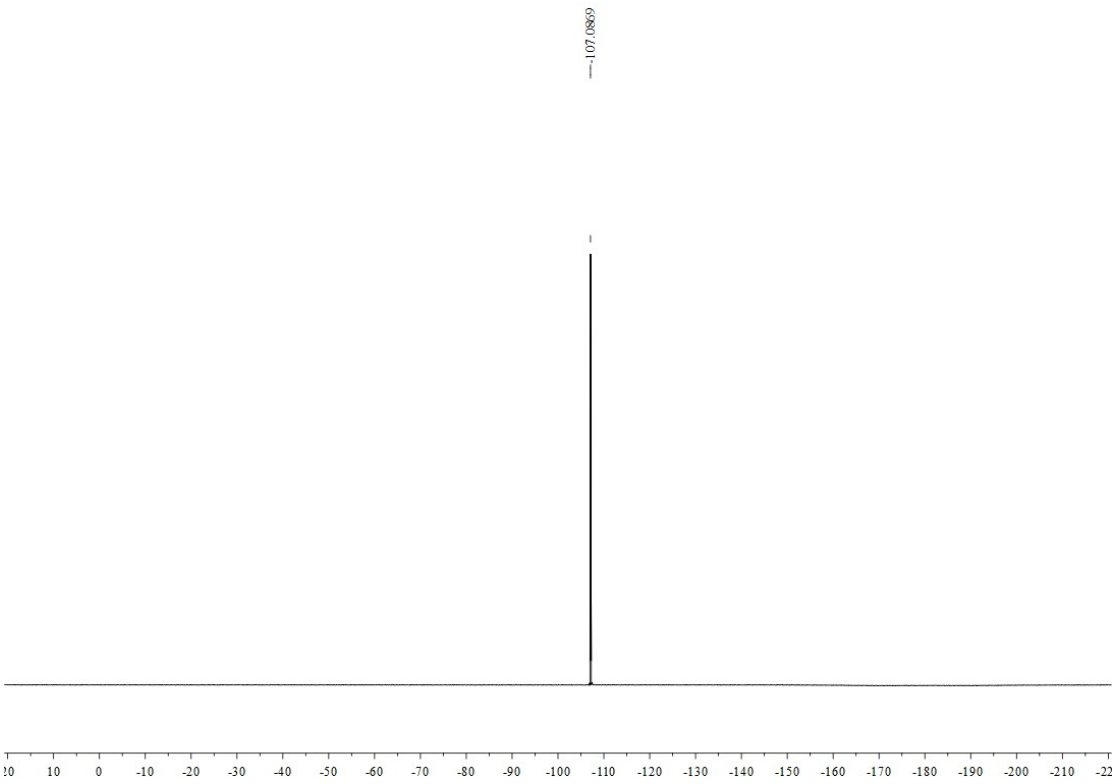
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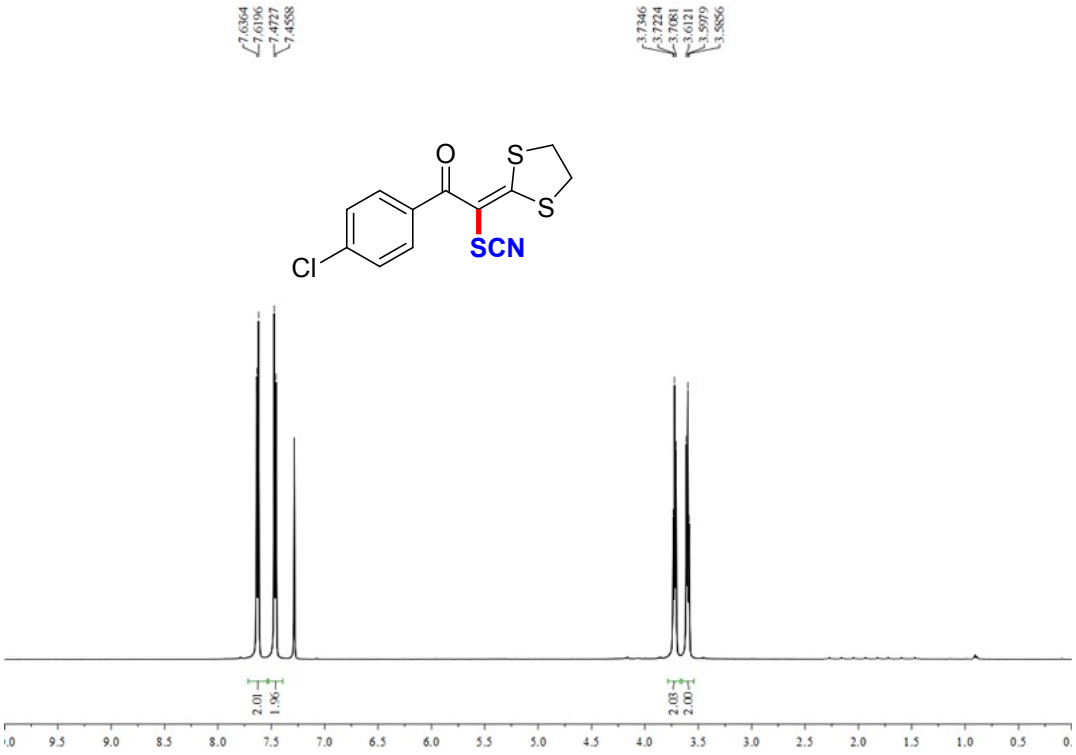
3fa

[1]HNMR



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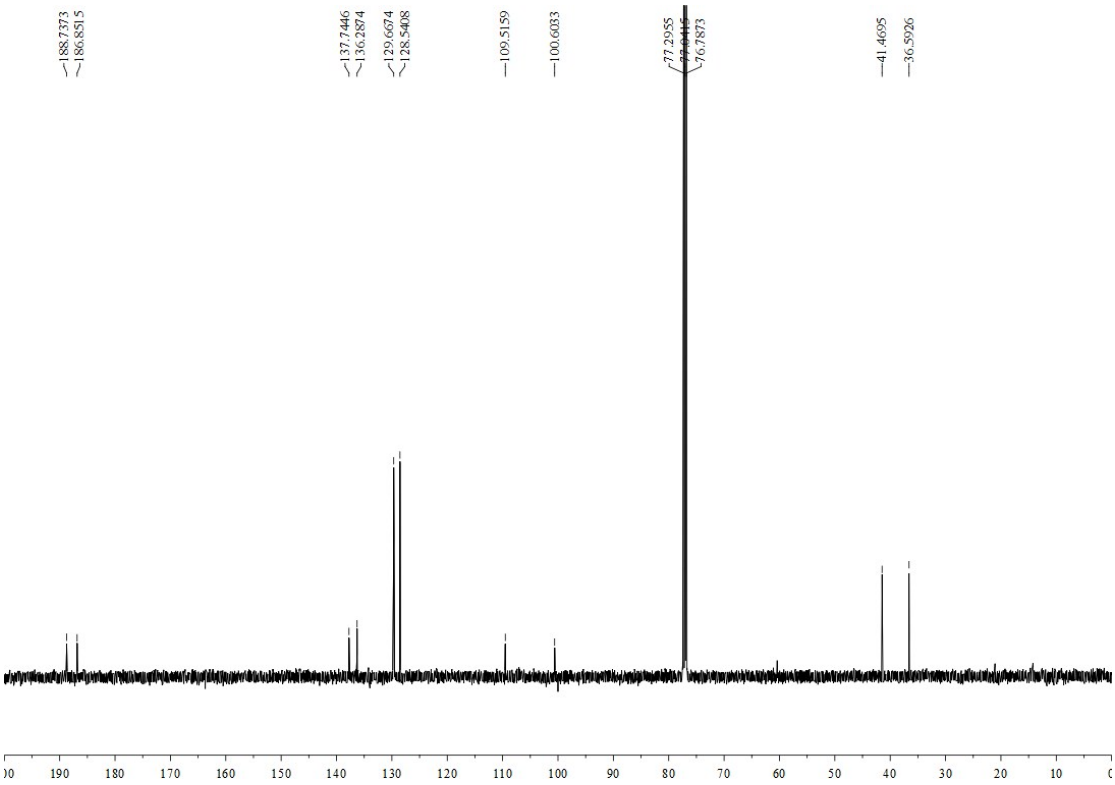

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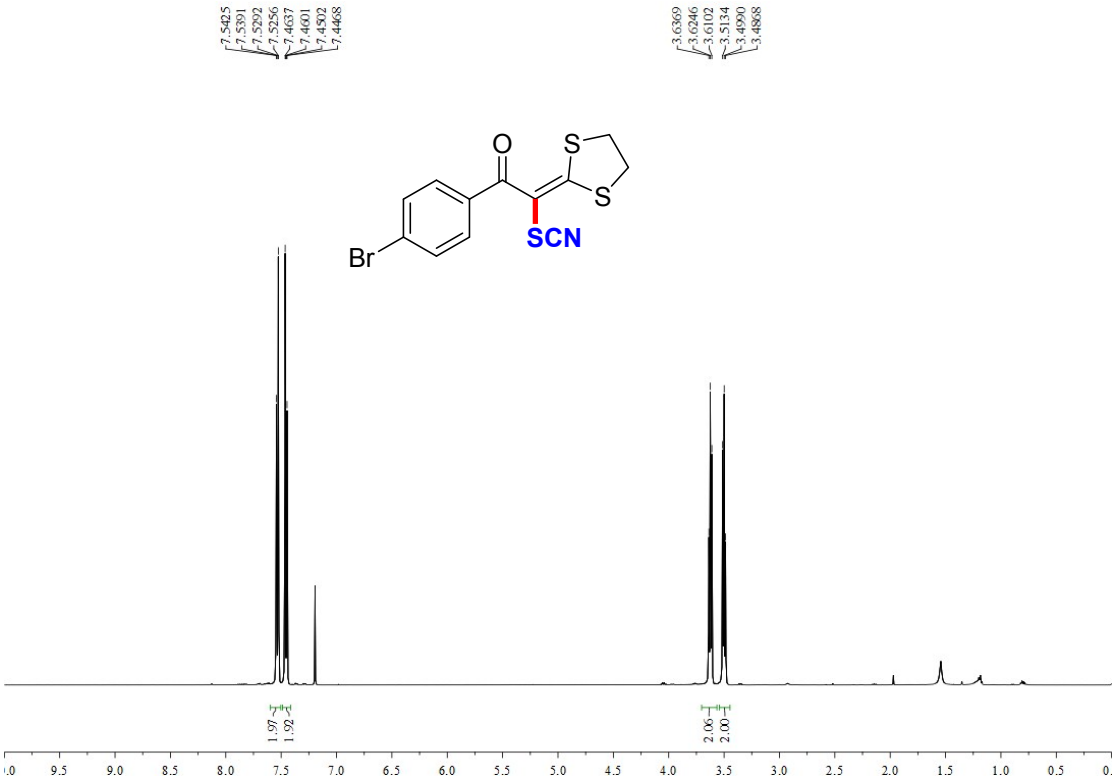

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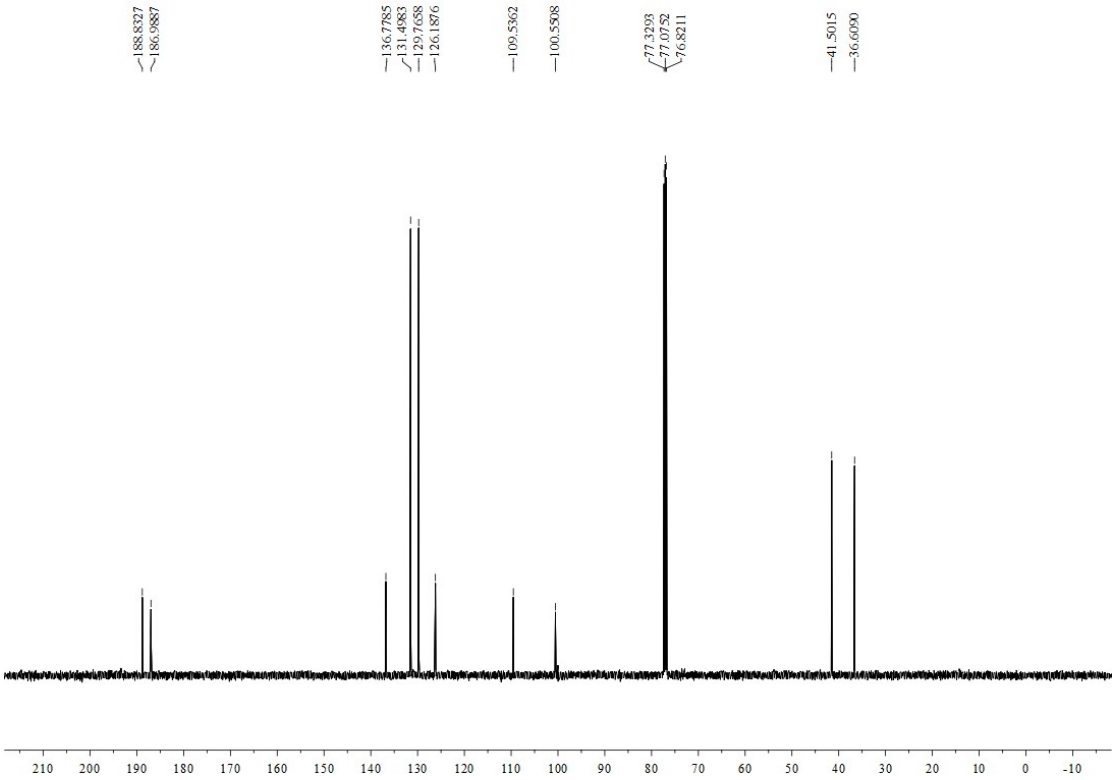

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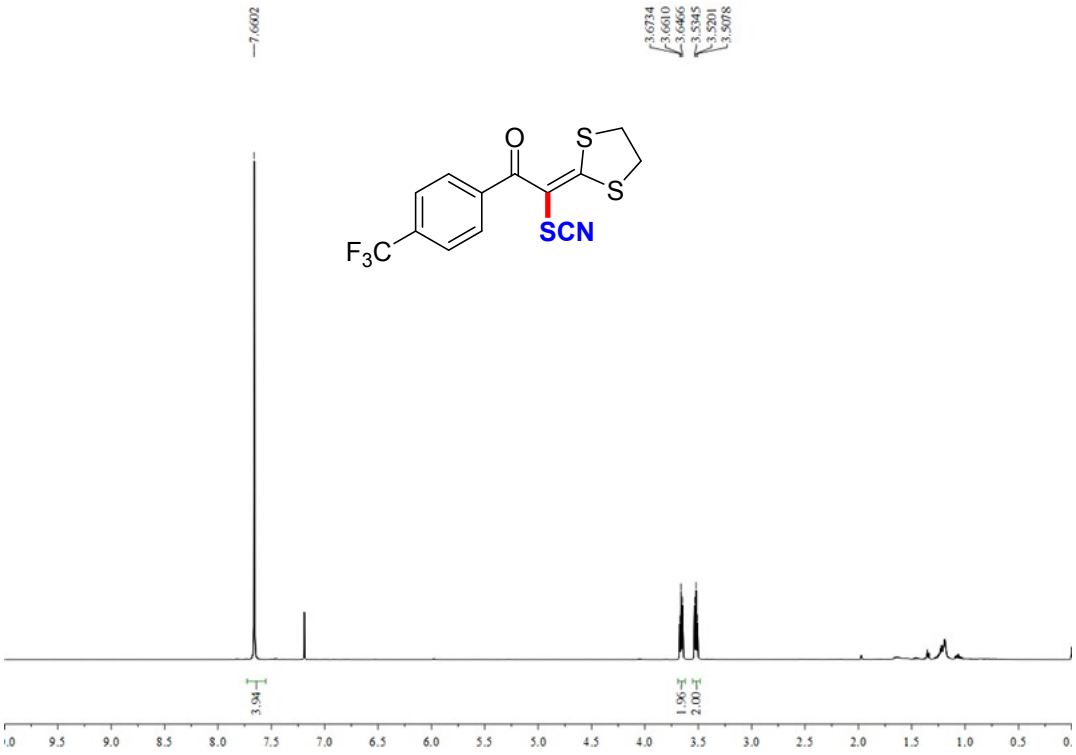

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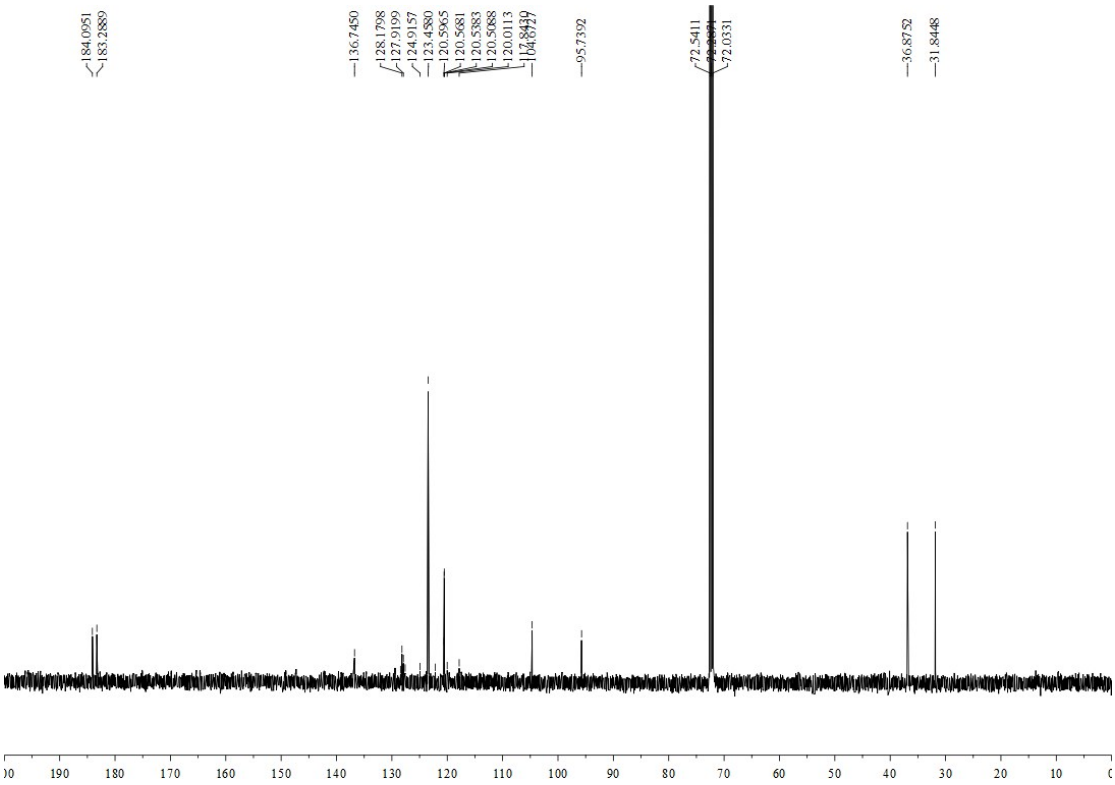

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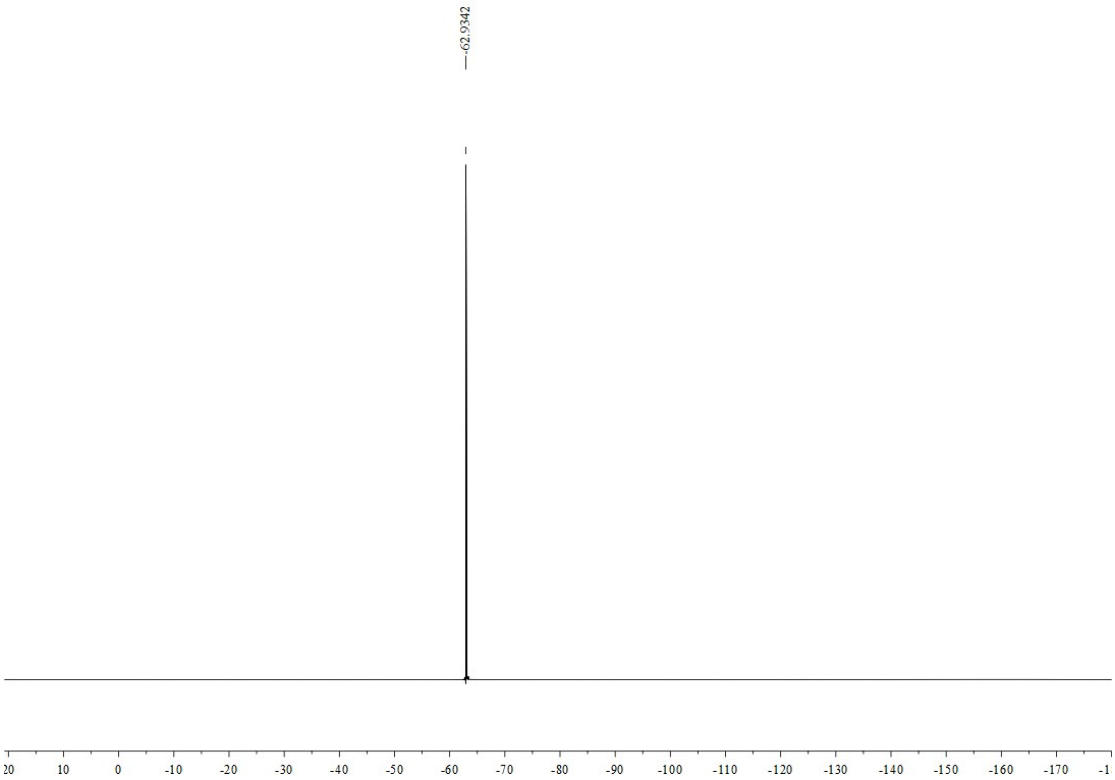
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3ia

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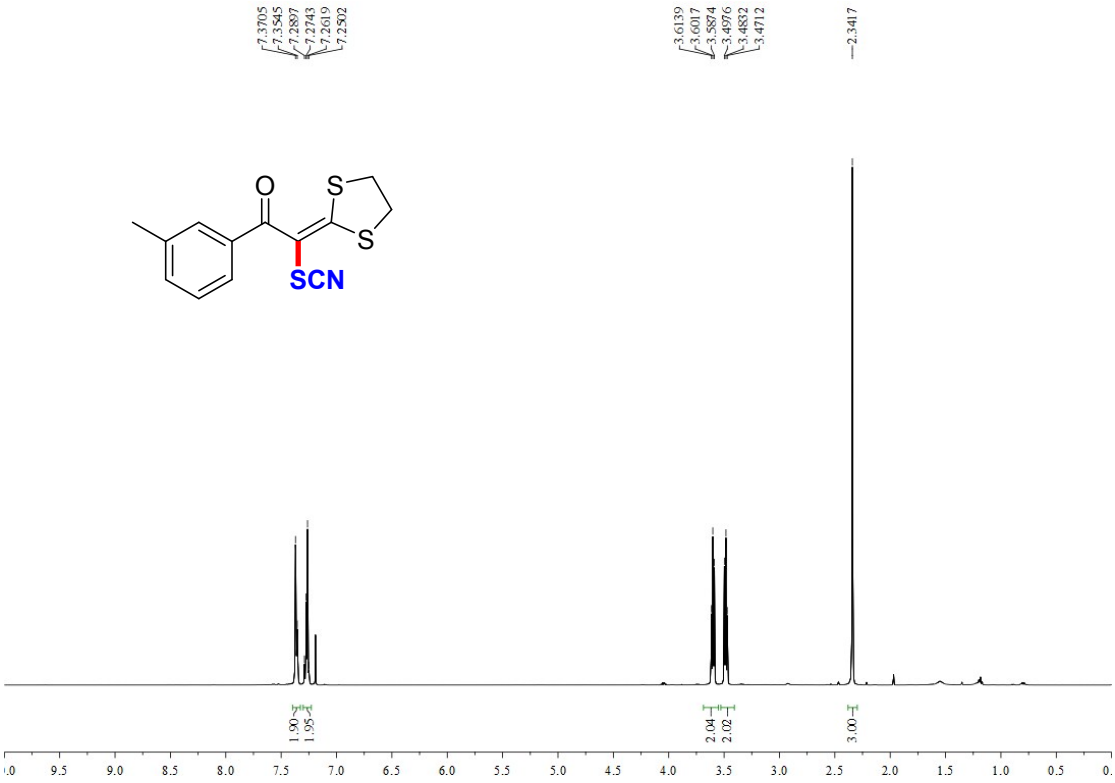

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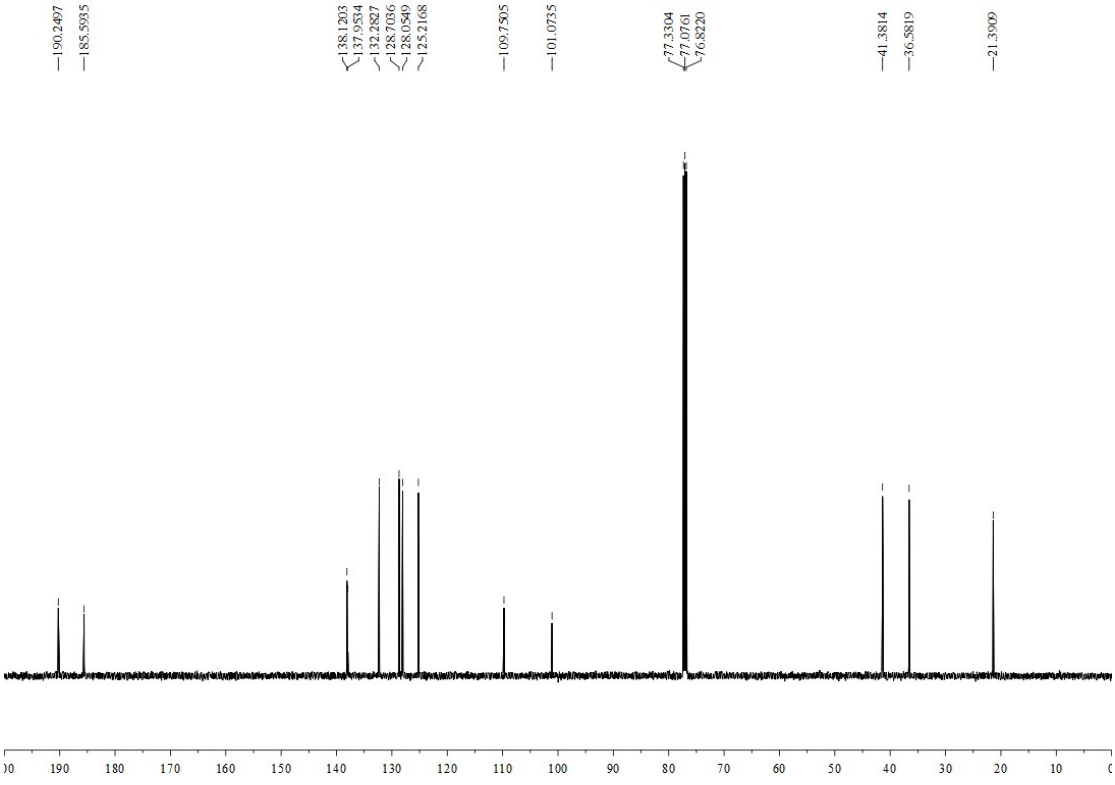

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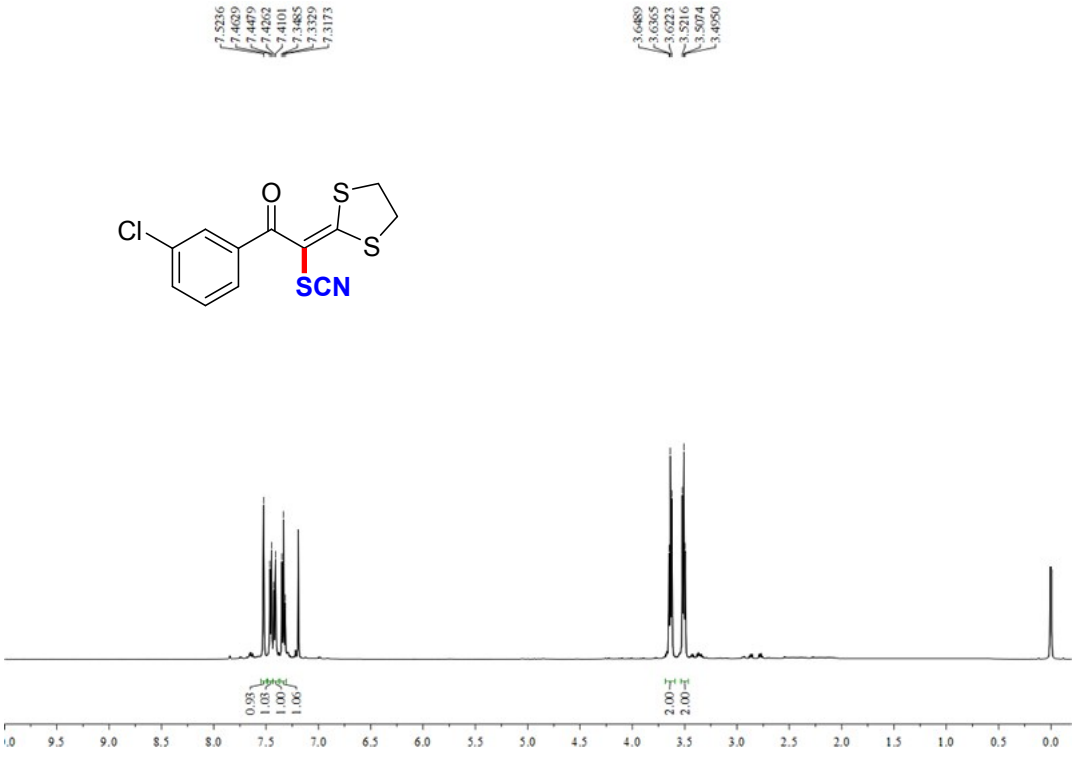

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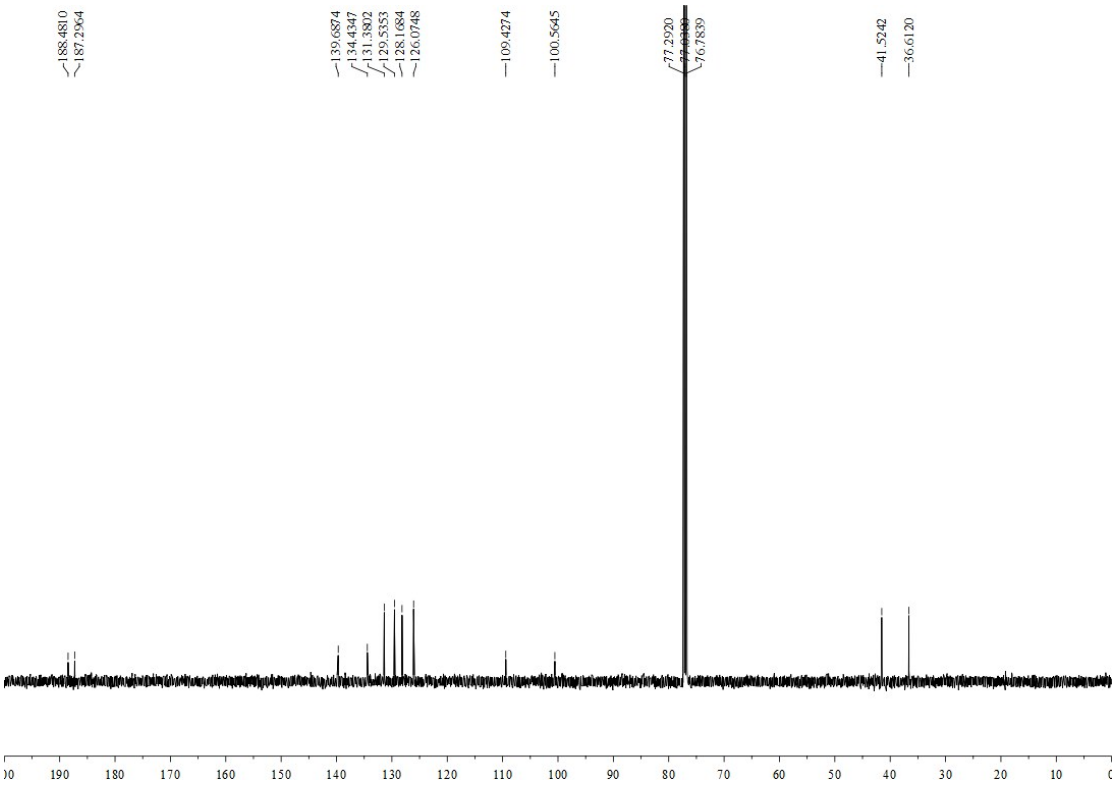

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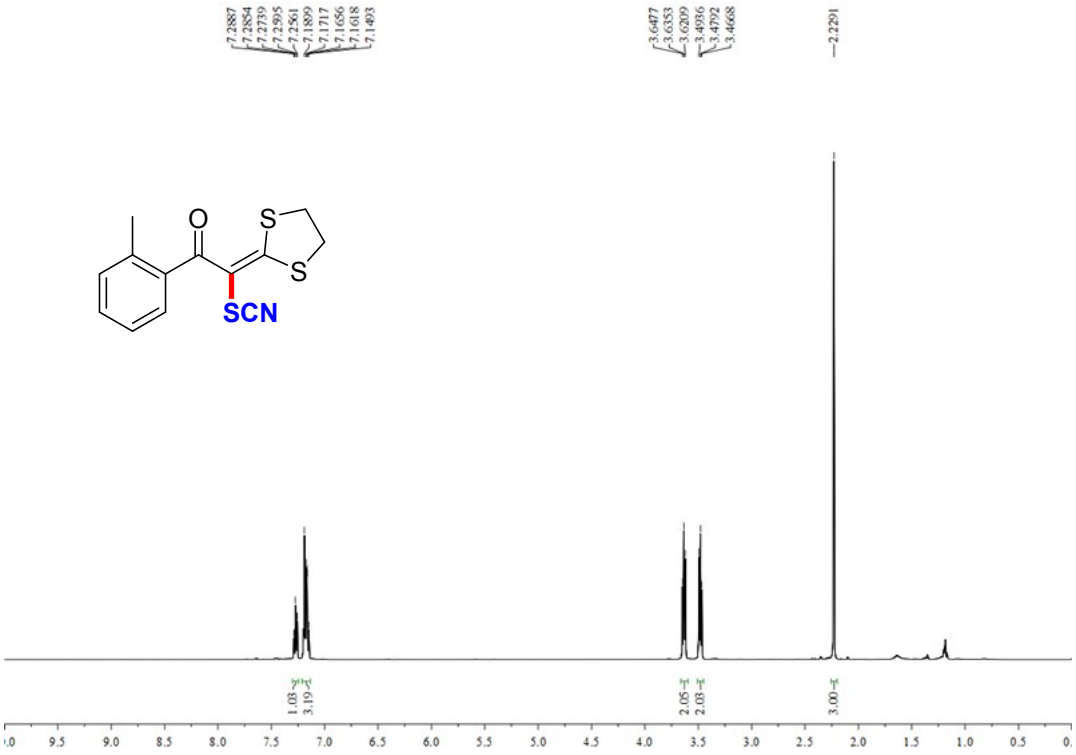

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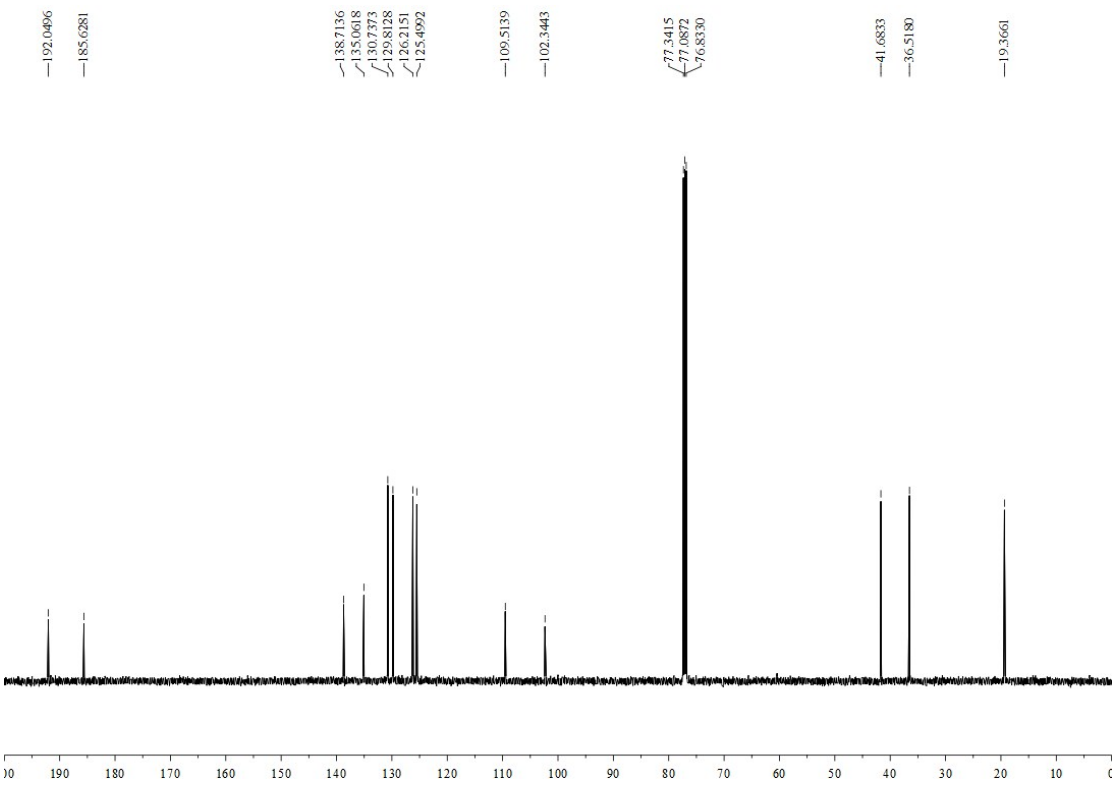

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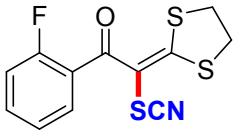

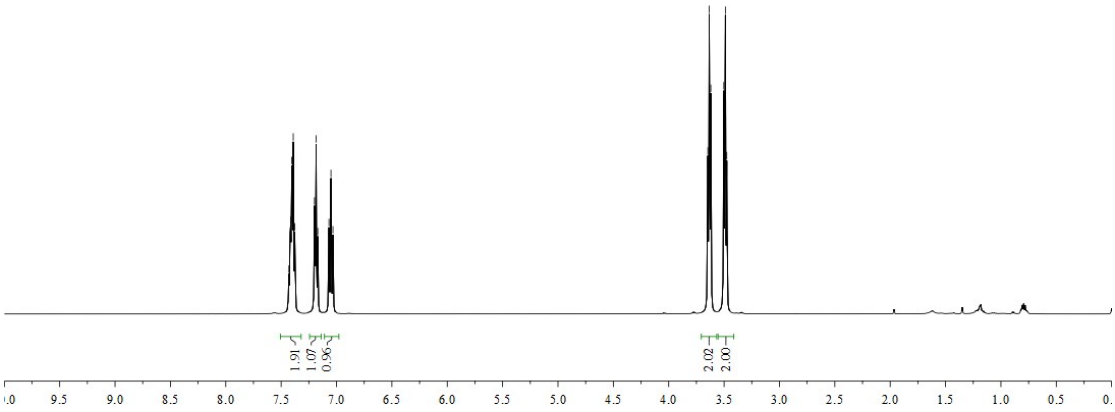

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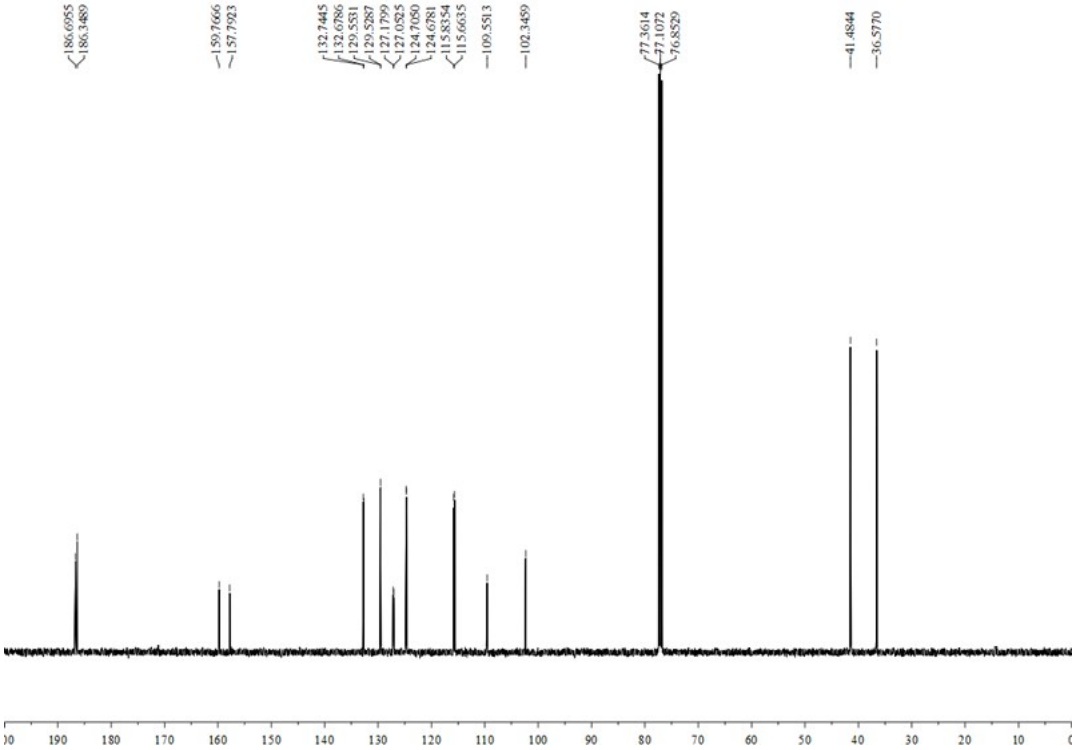
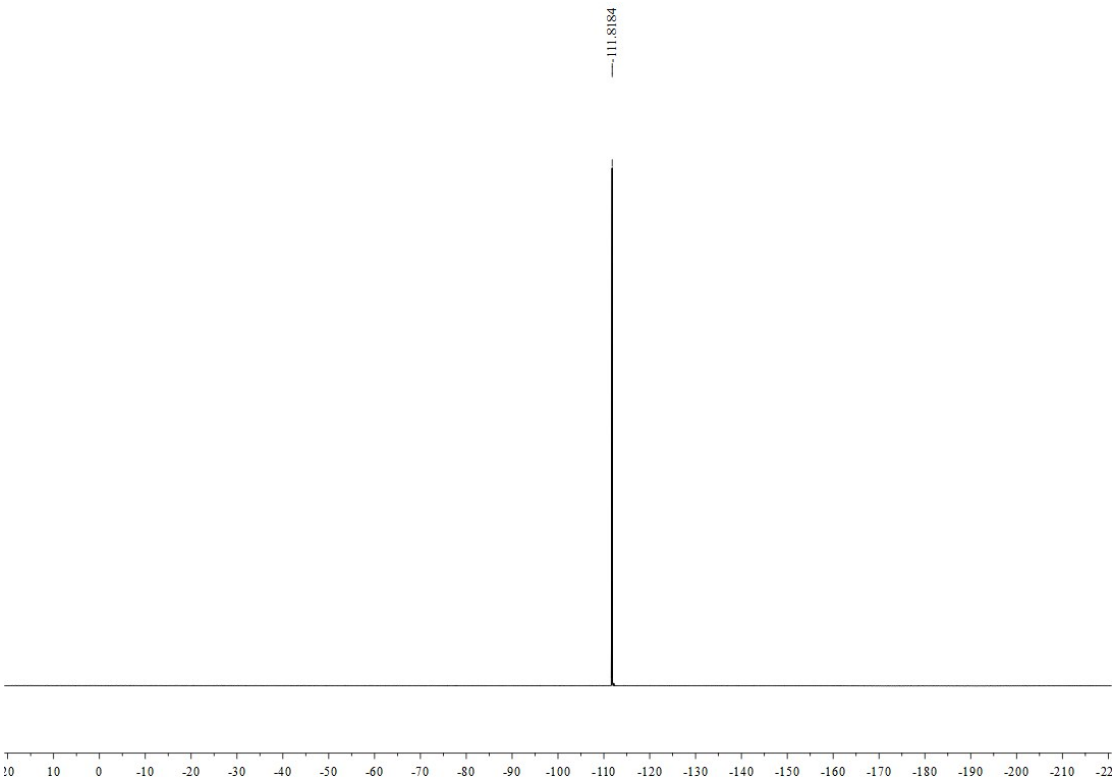


^{19}FNMR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3ma

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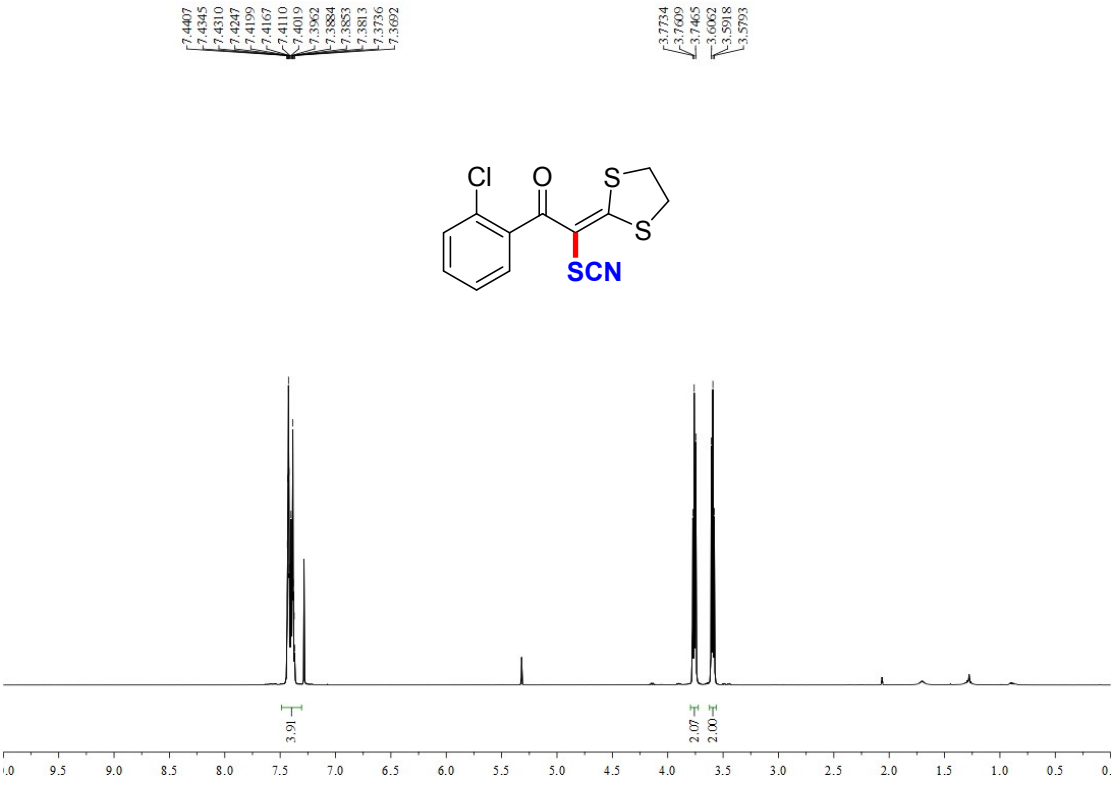

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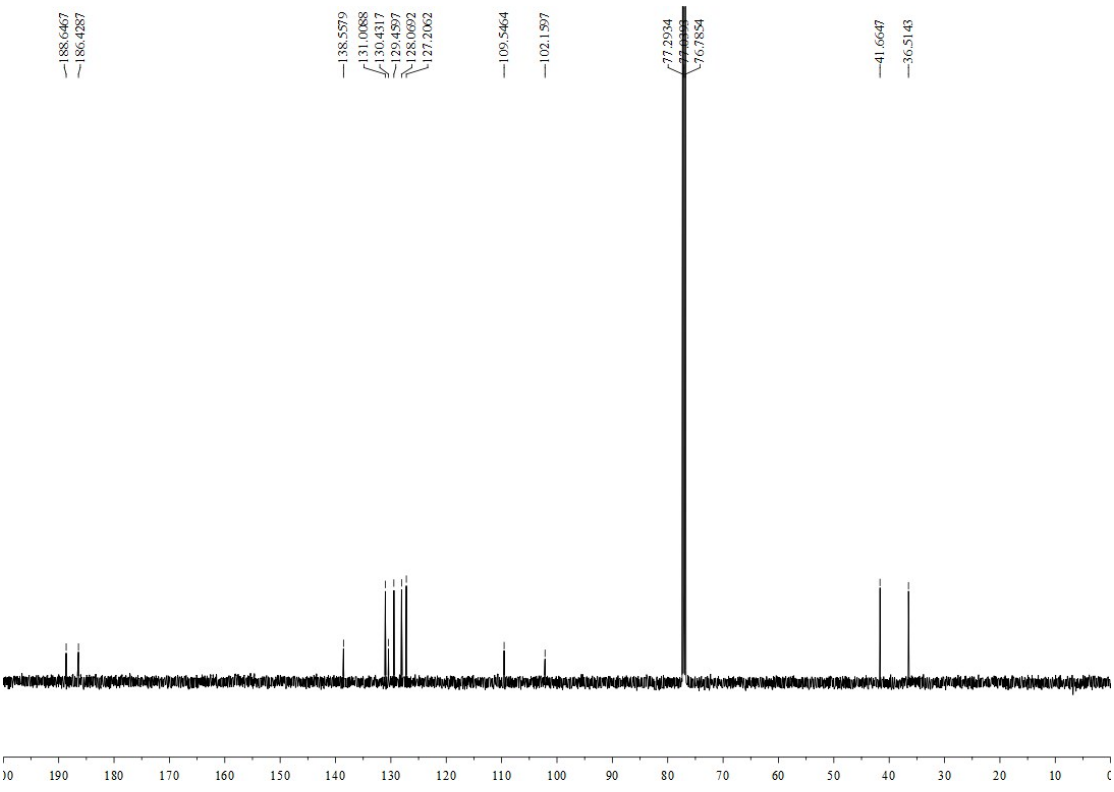

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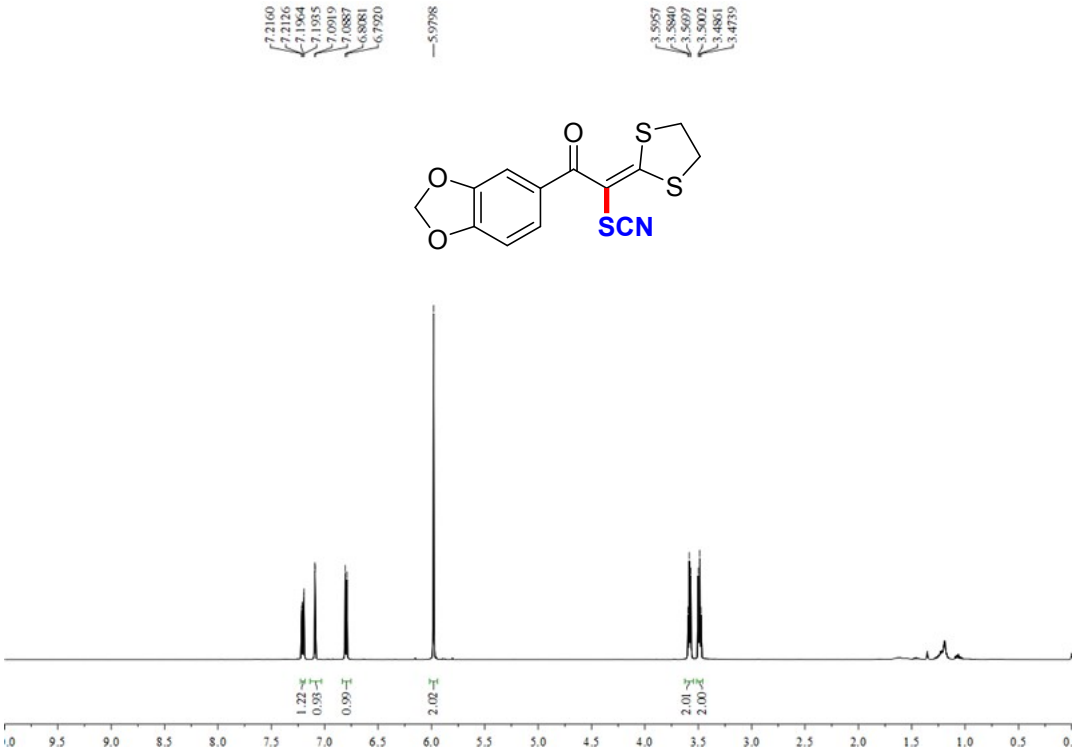

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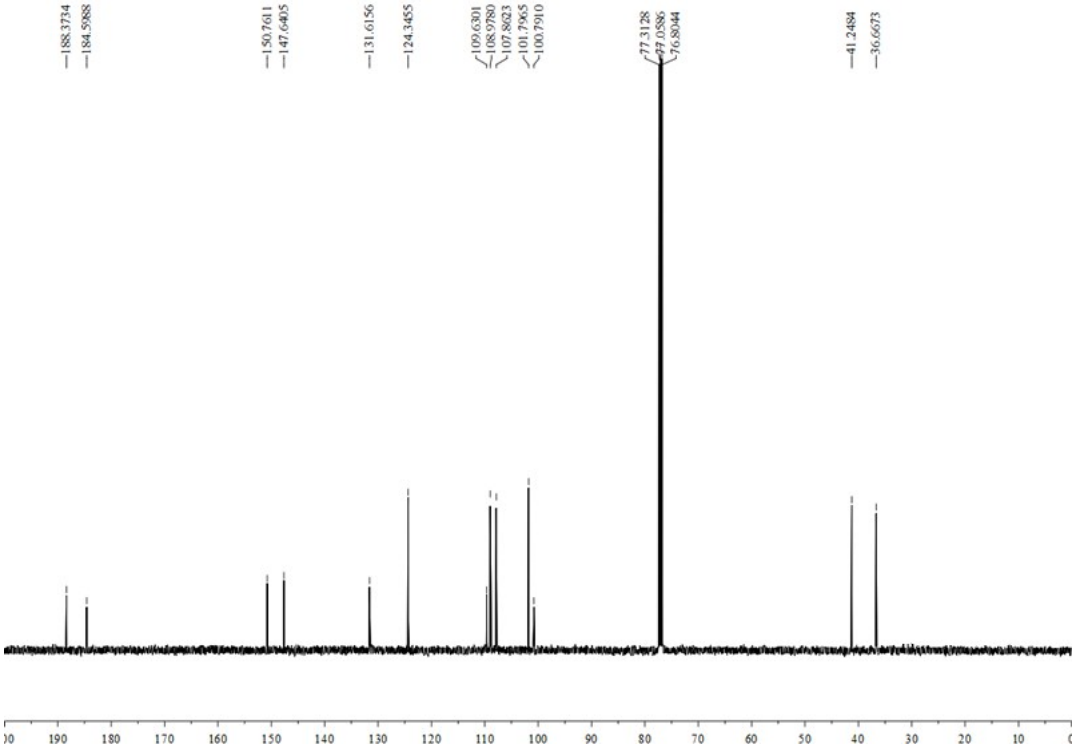

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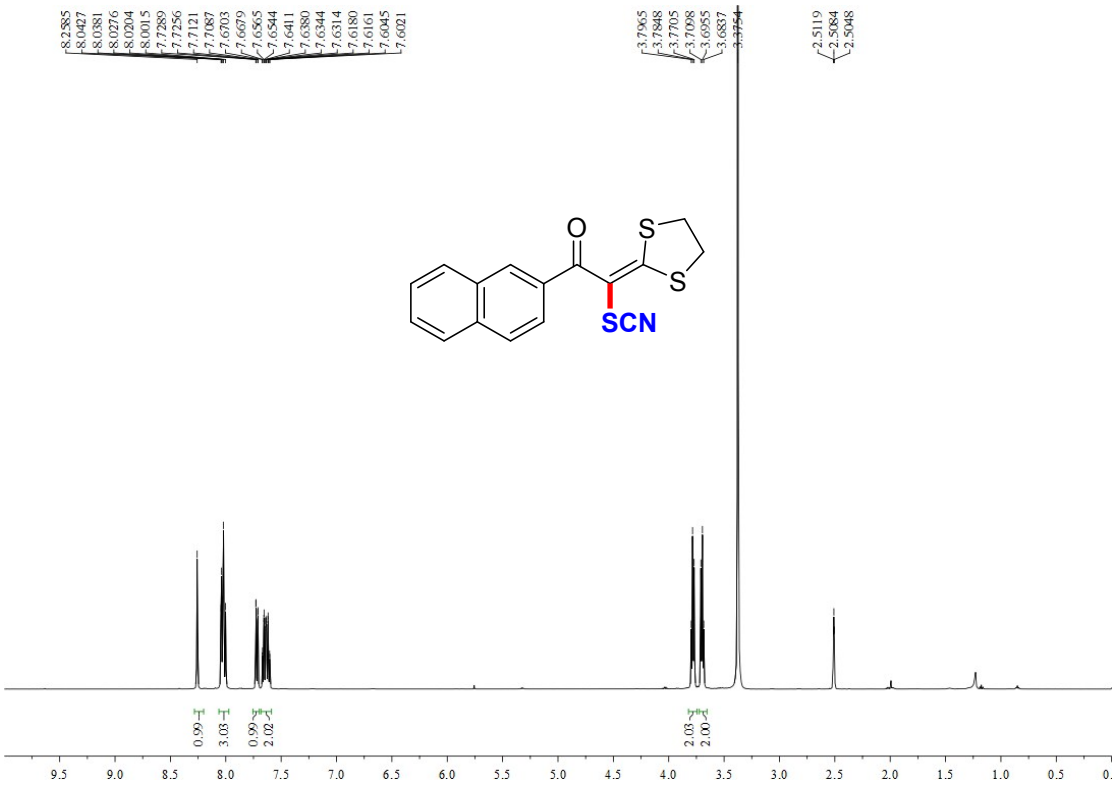

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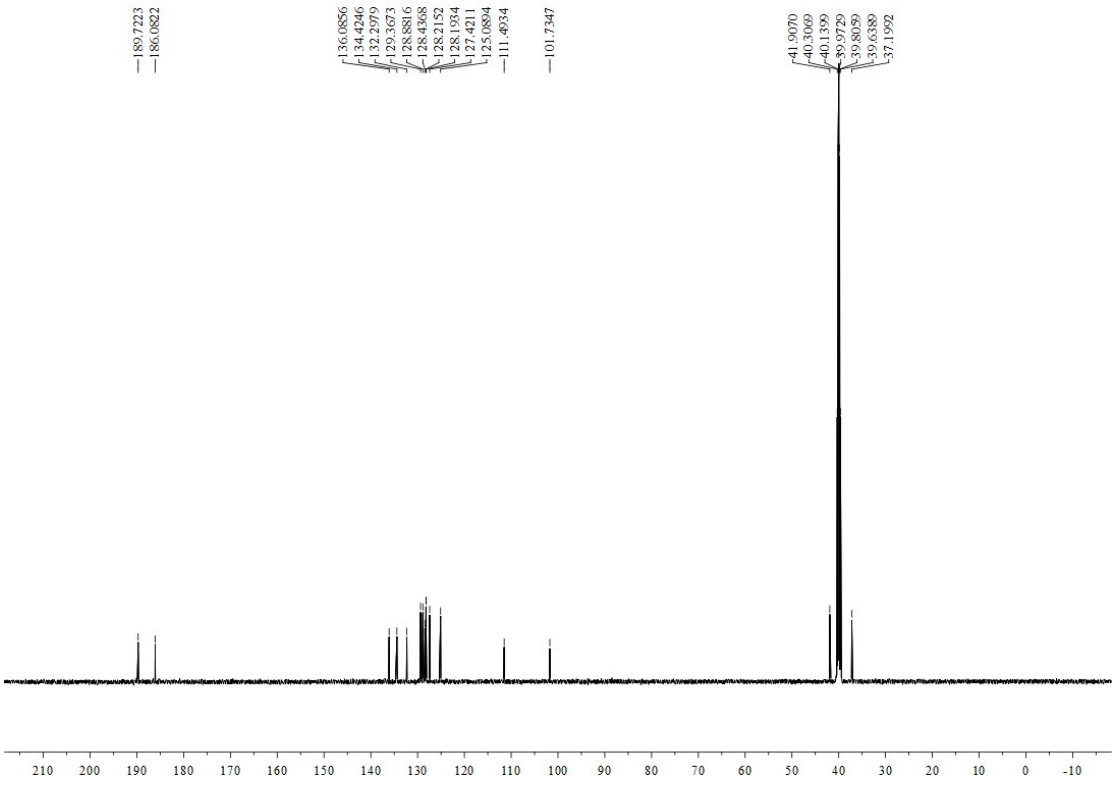

3pa

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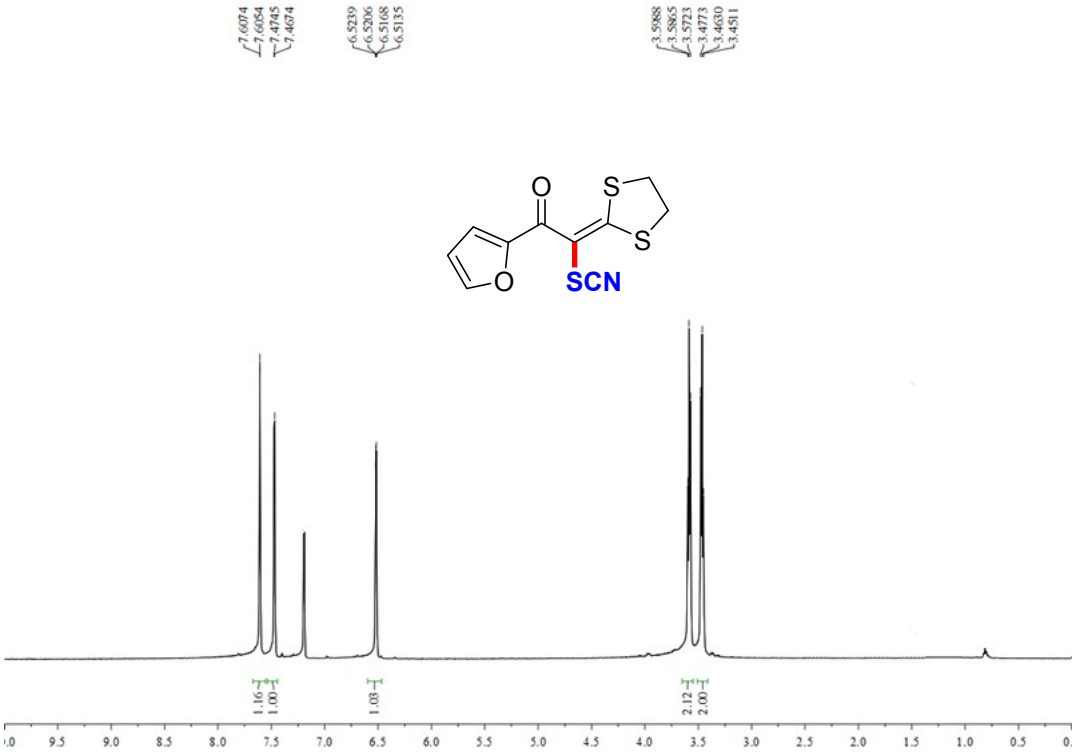

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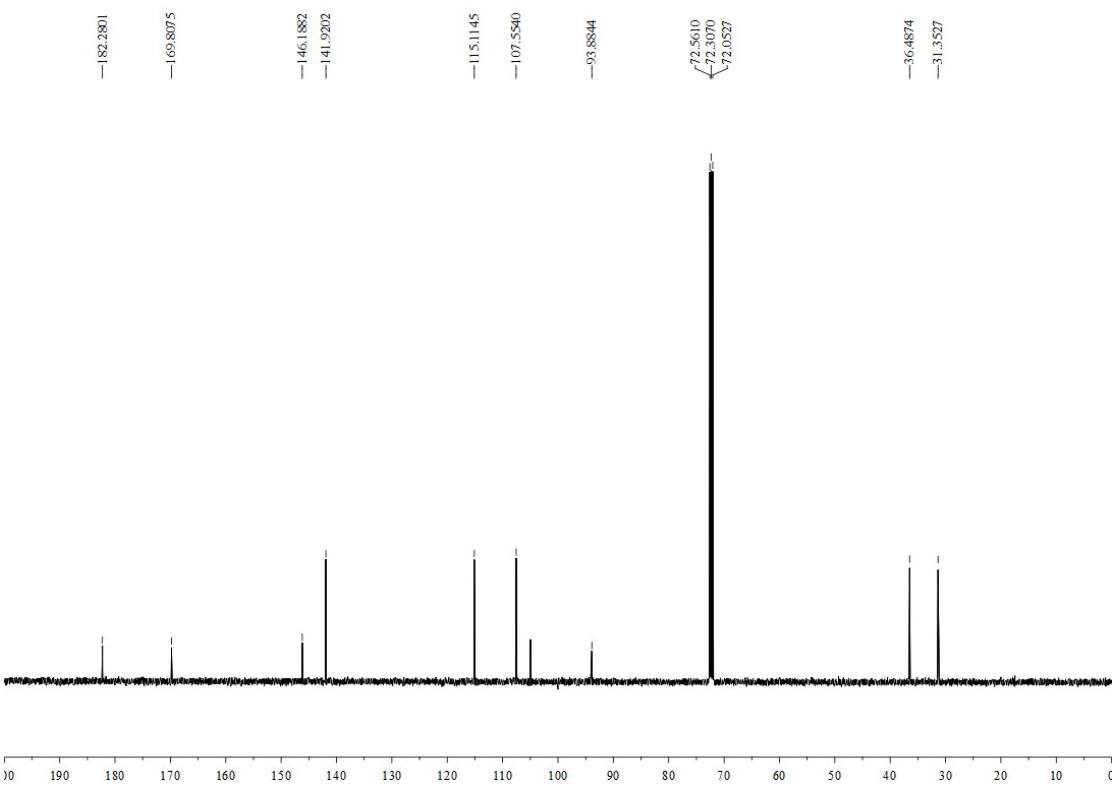

3qa

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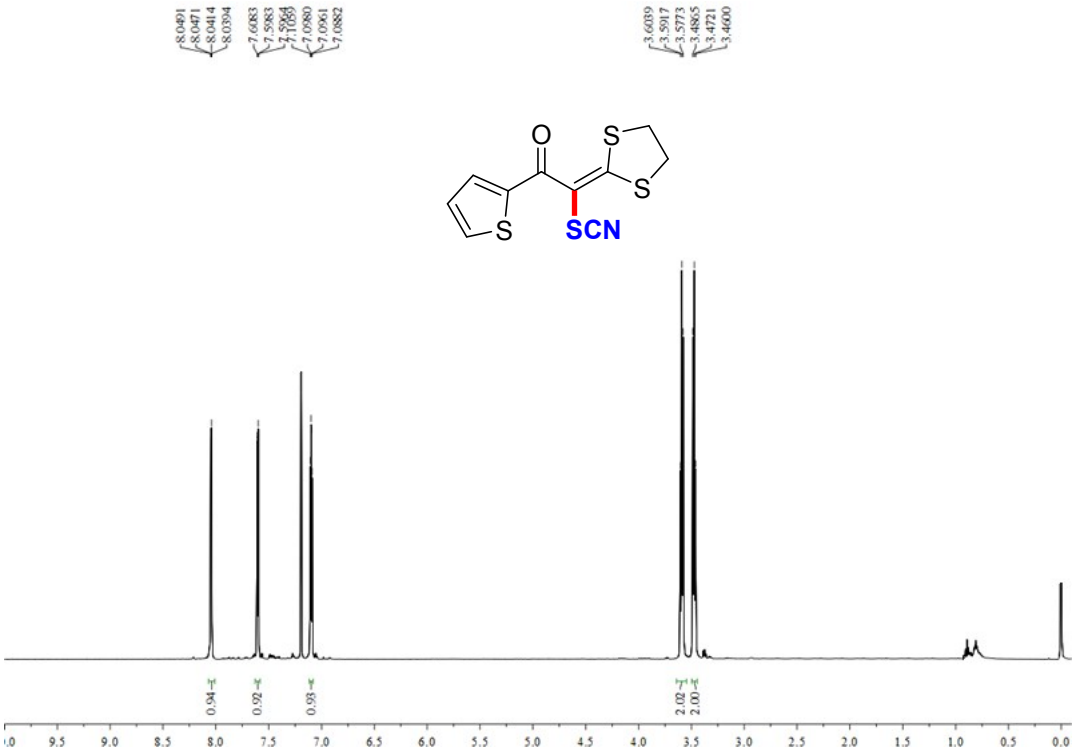

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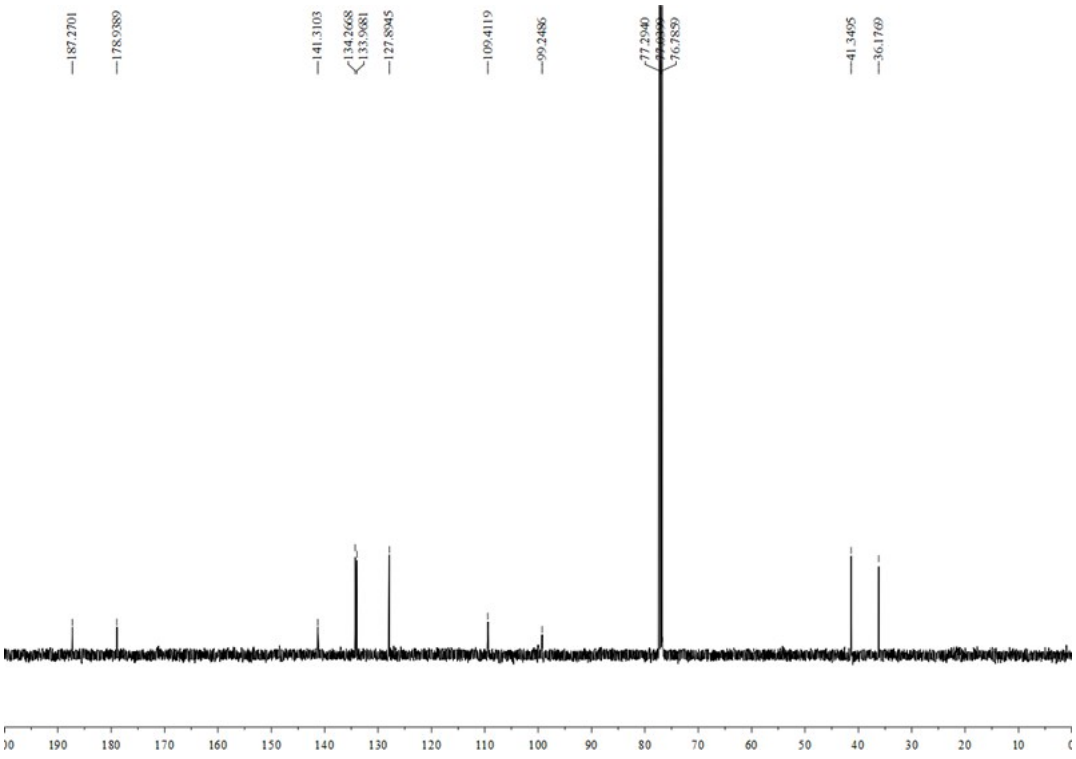

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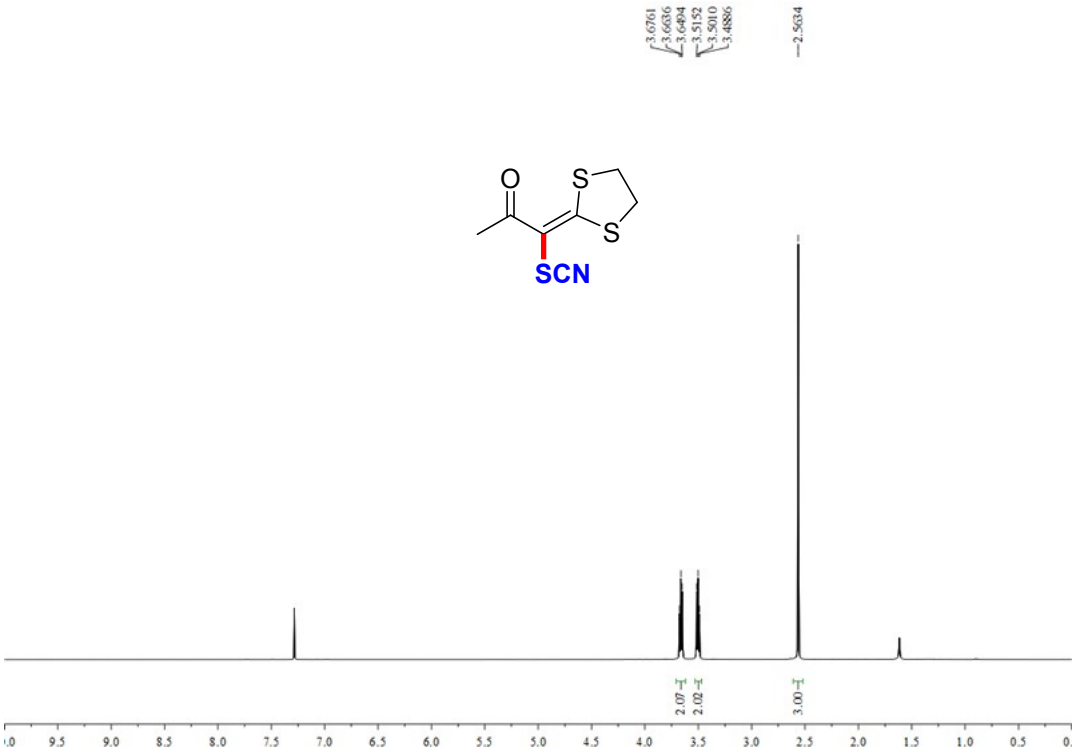

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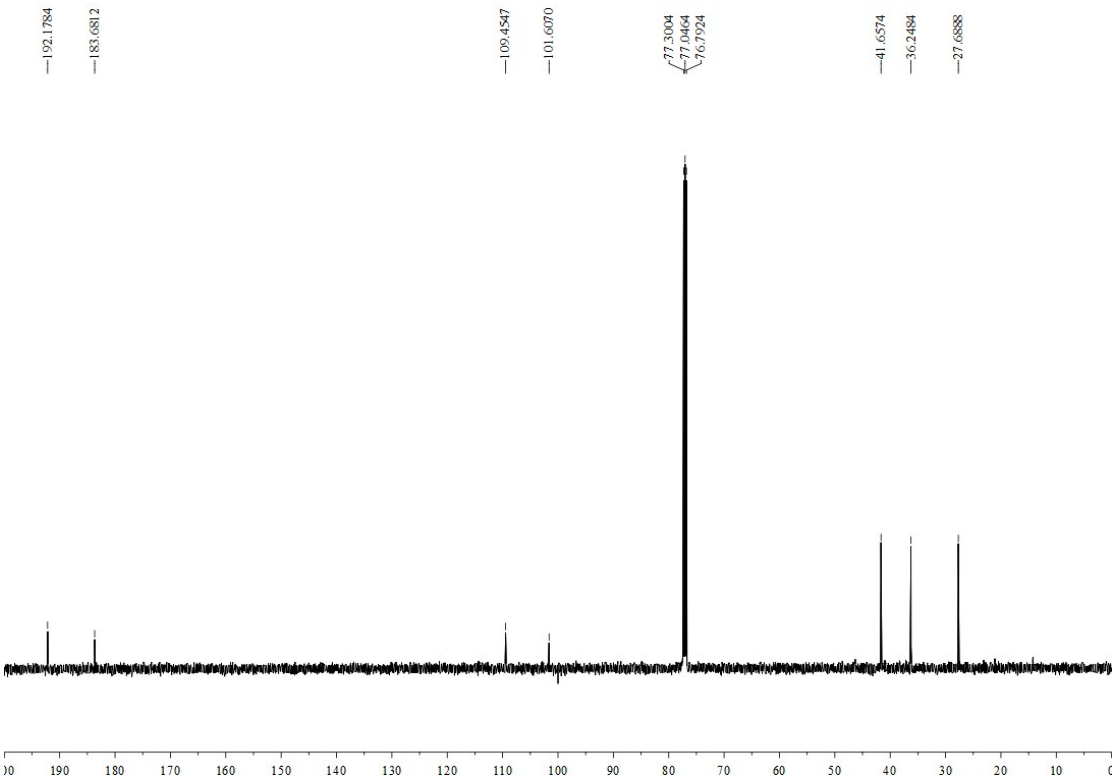

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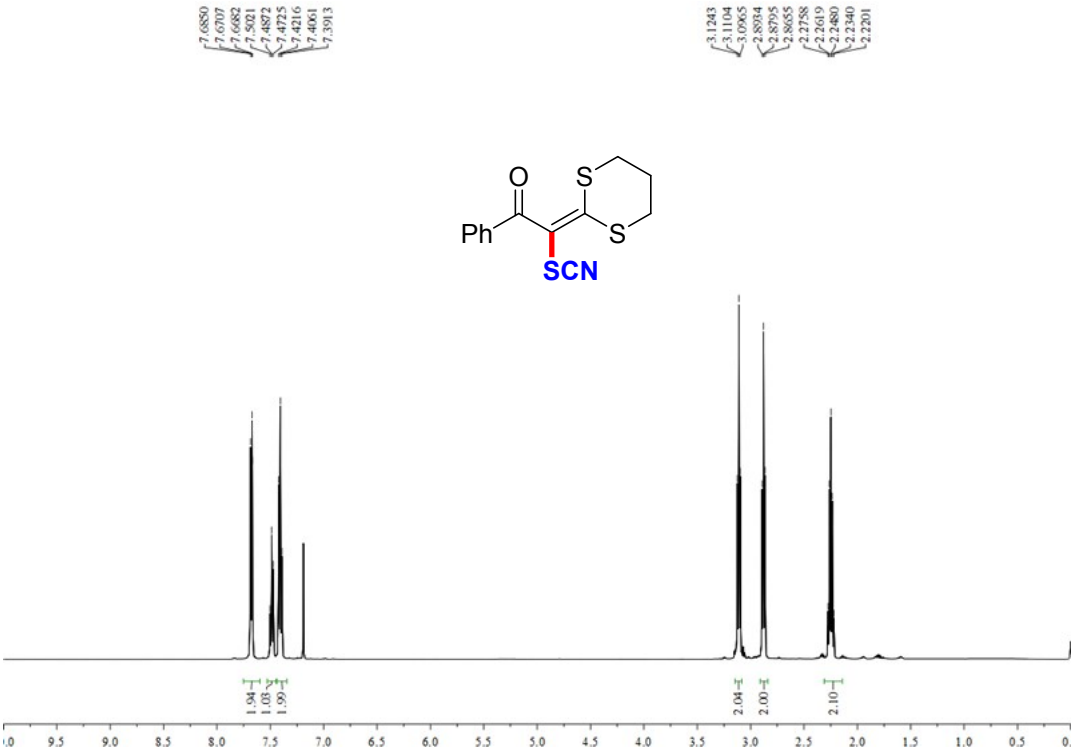

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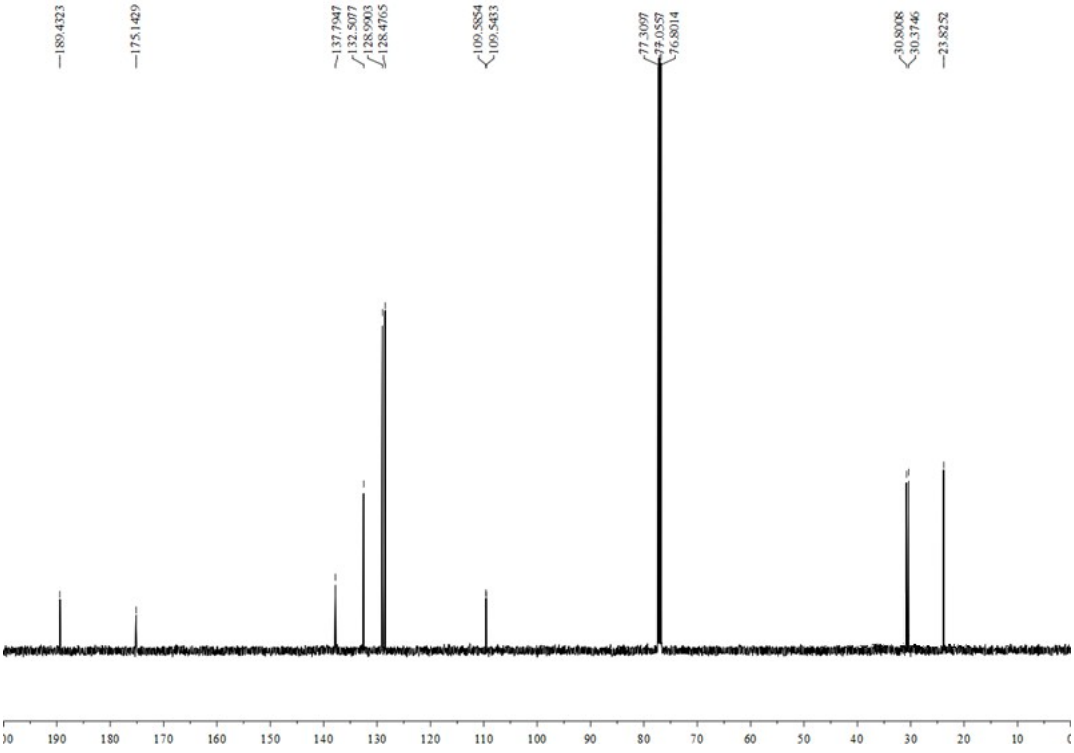

4a

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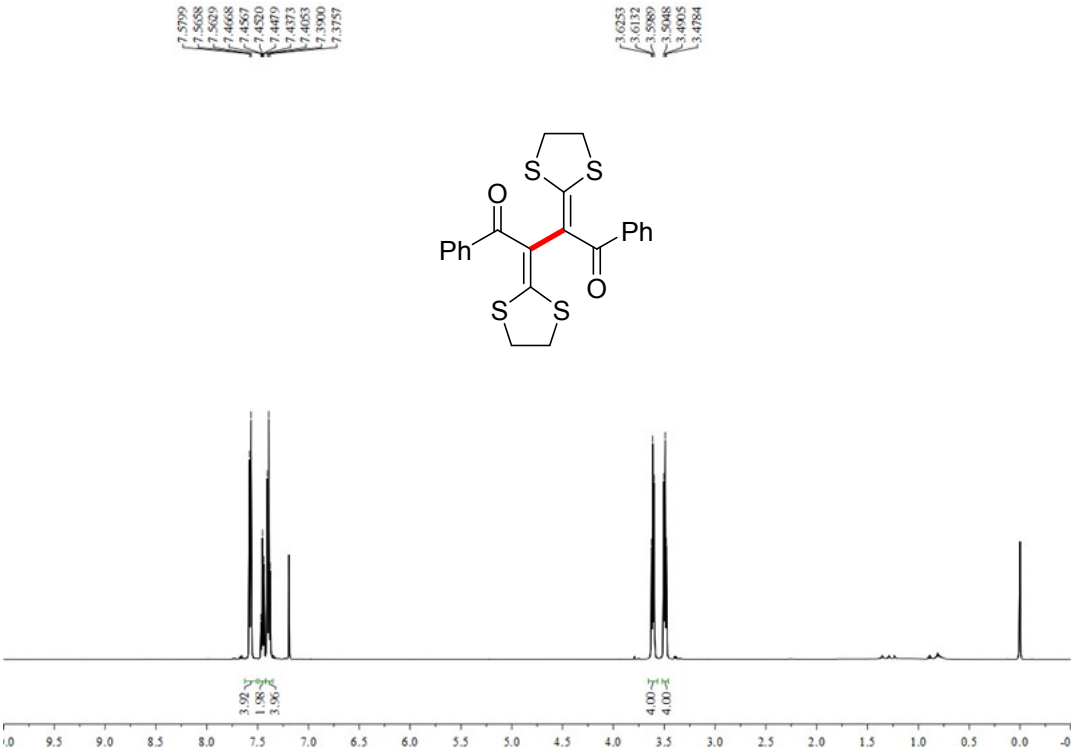

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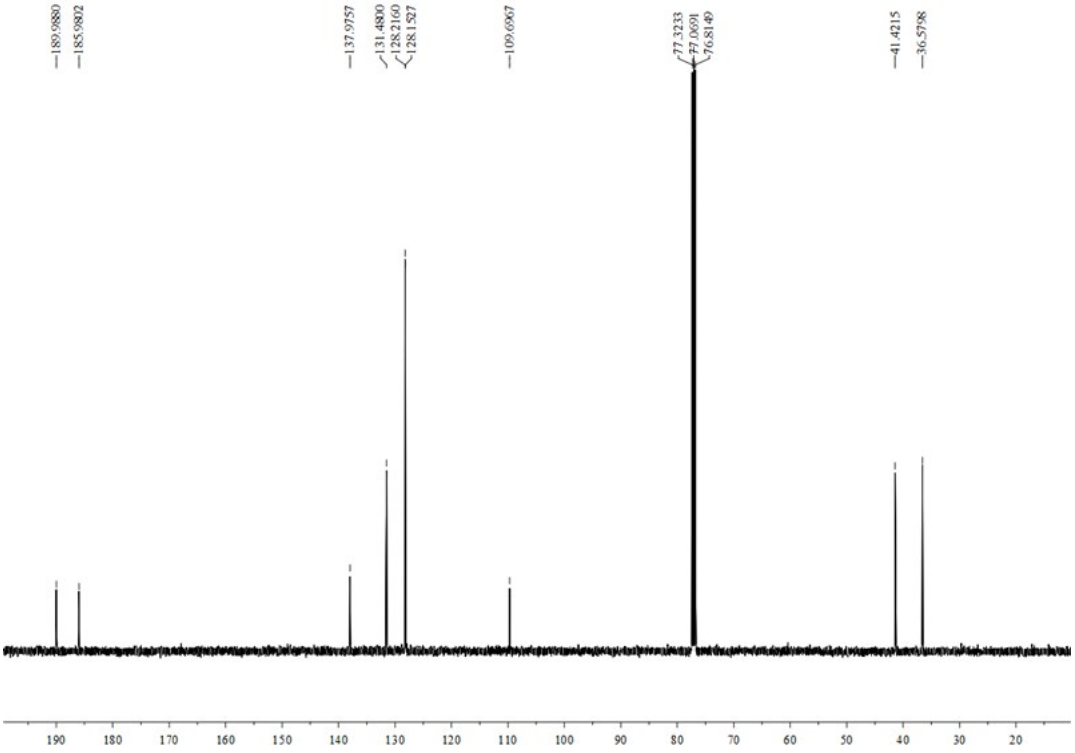

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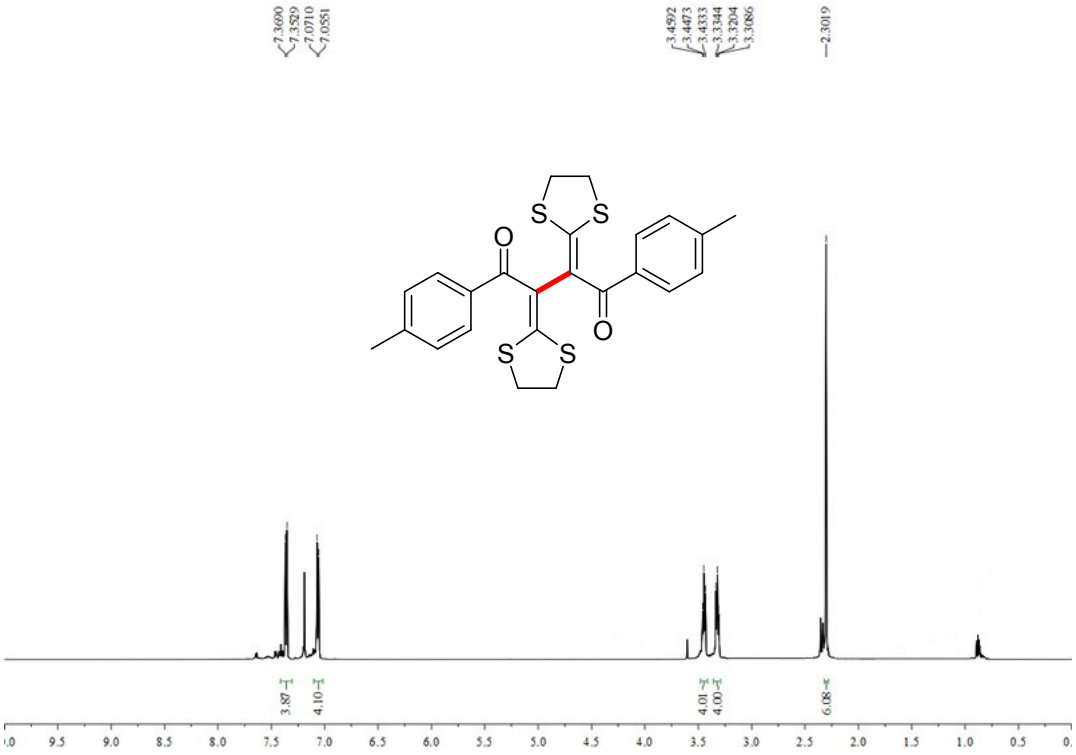

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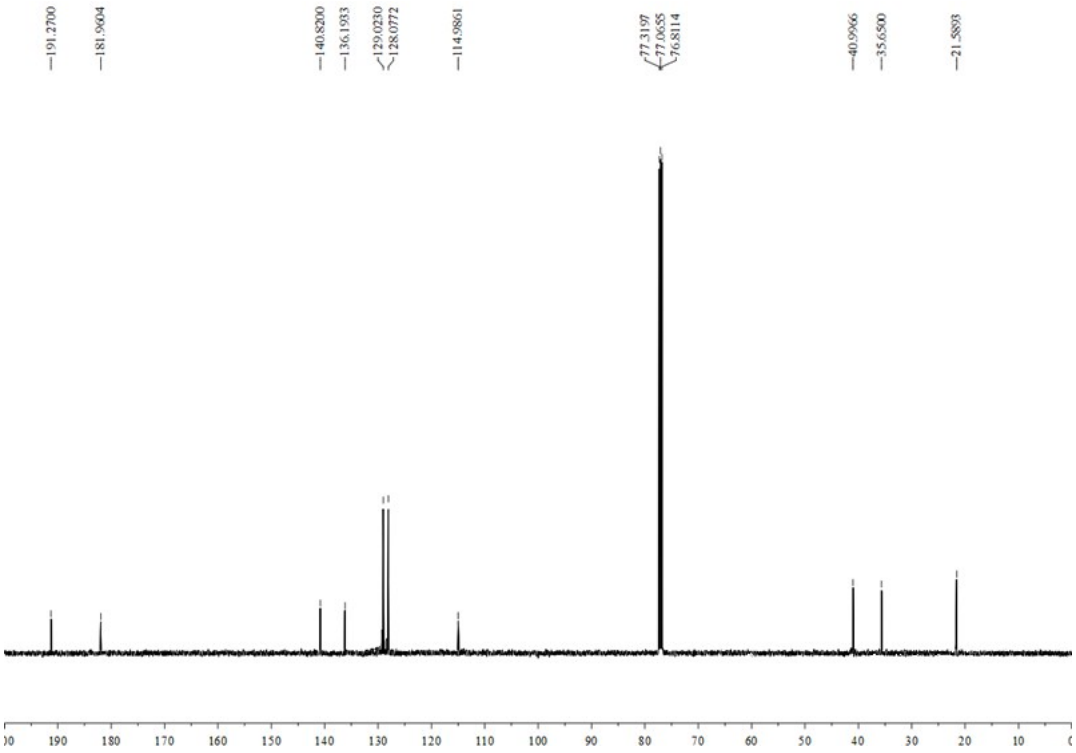

4c

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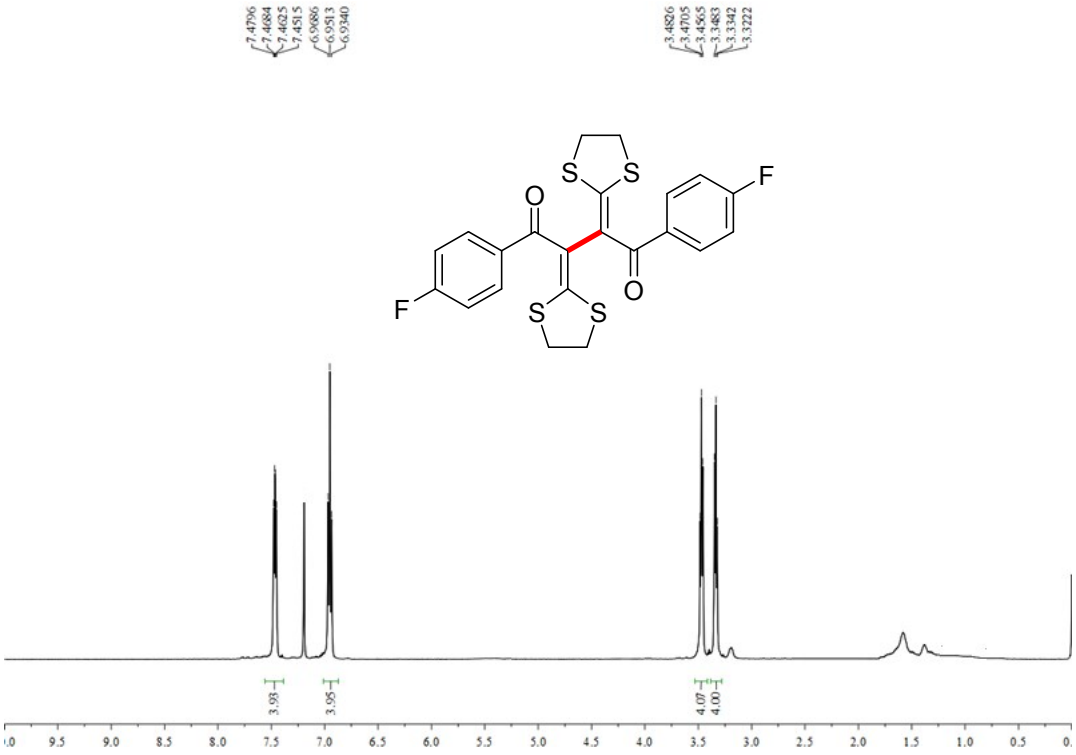

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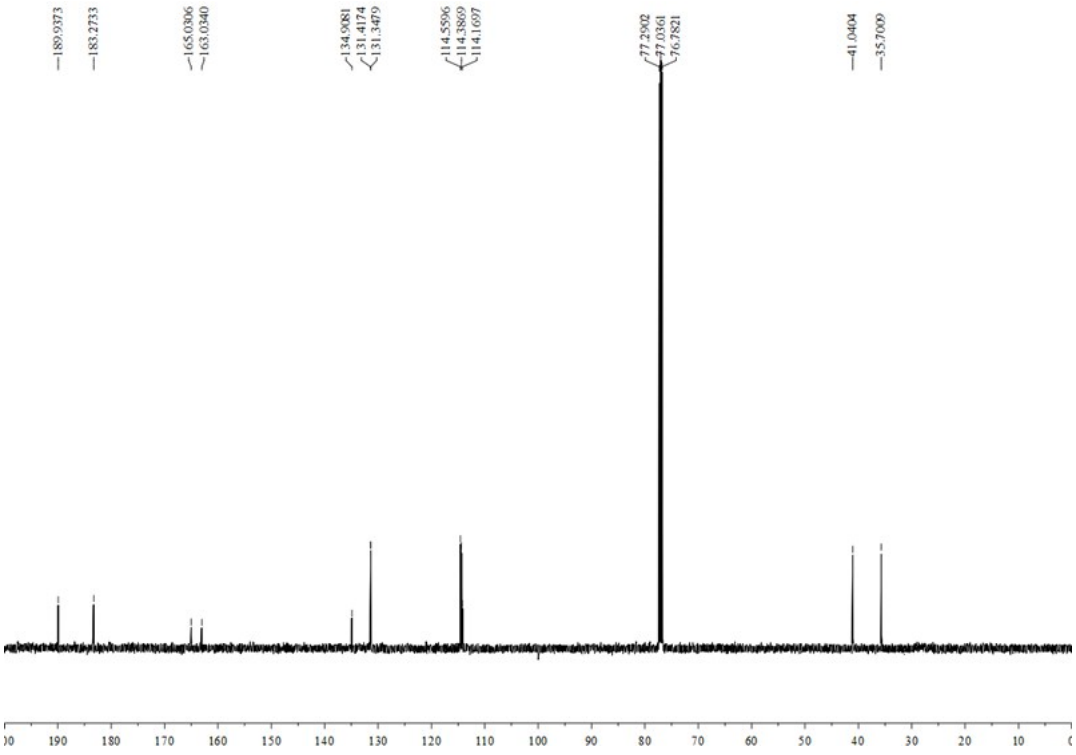
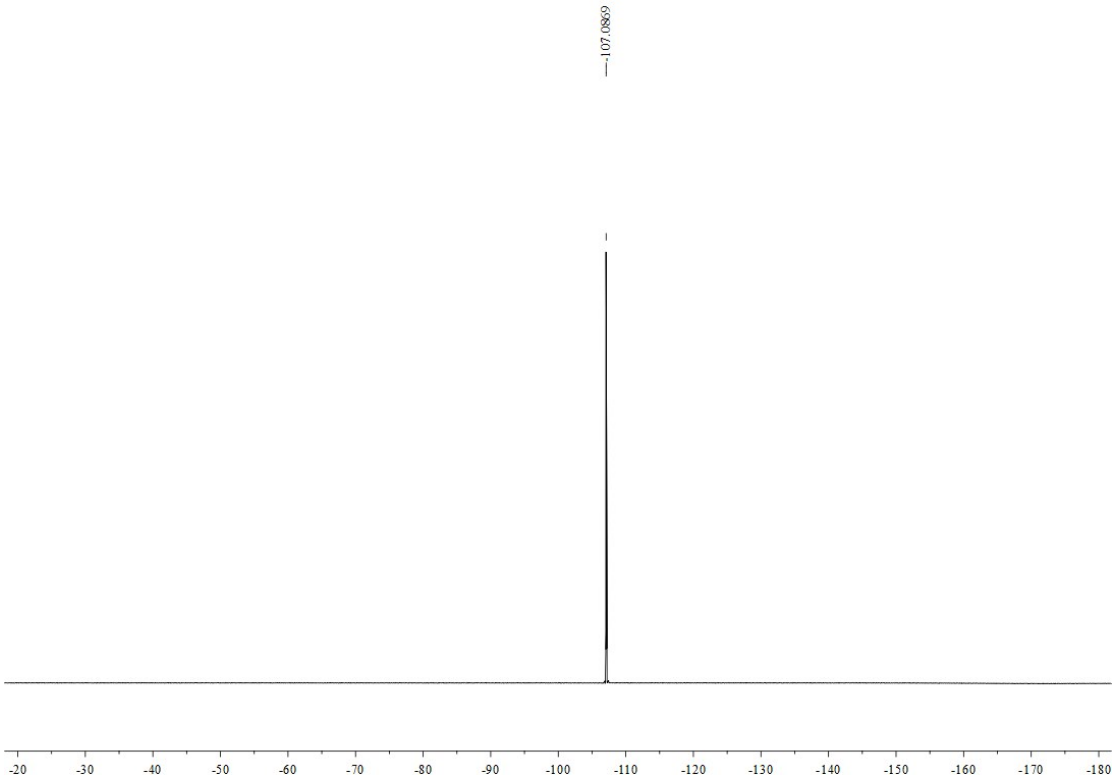


^{19}FNMR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4d

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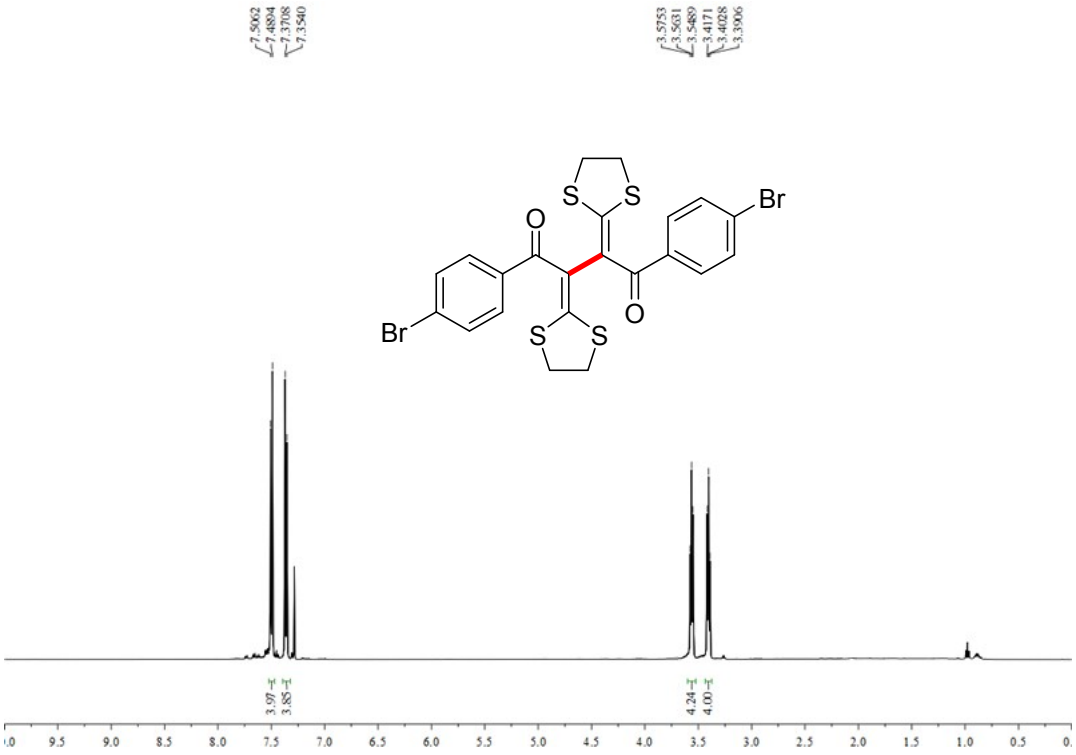

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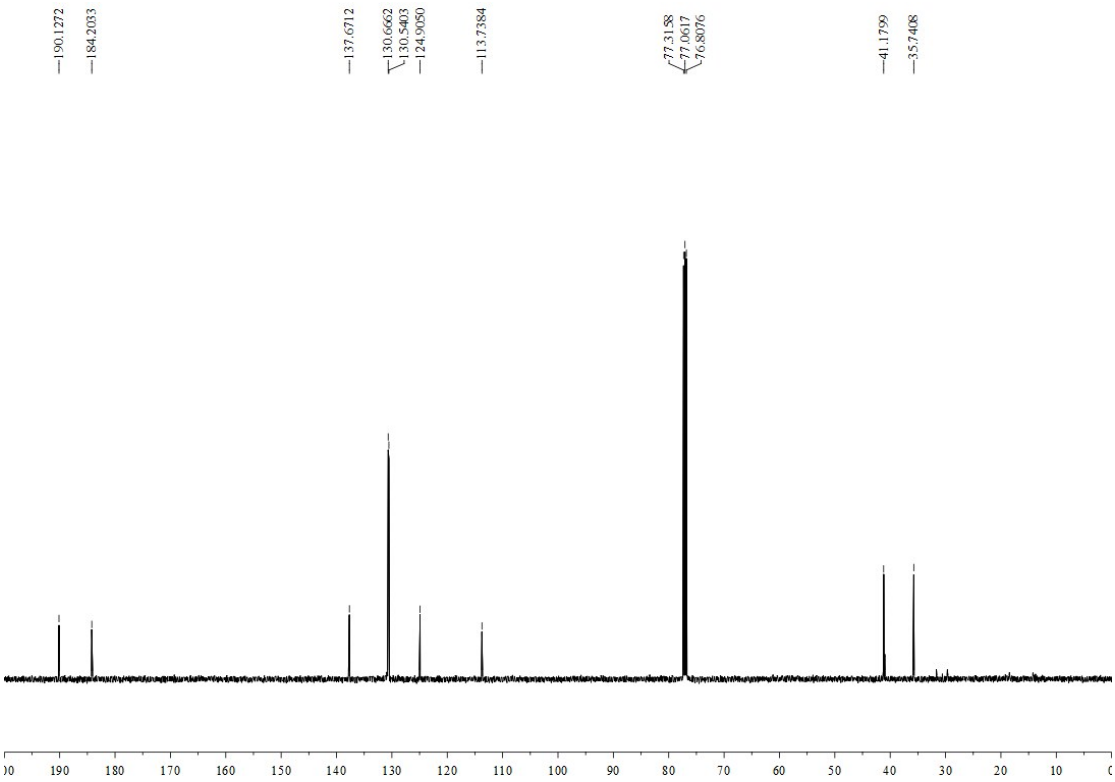

4e

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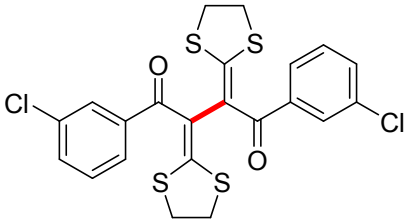

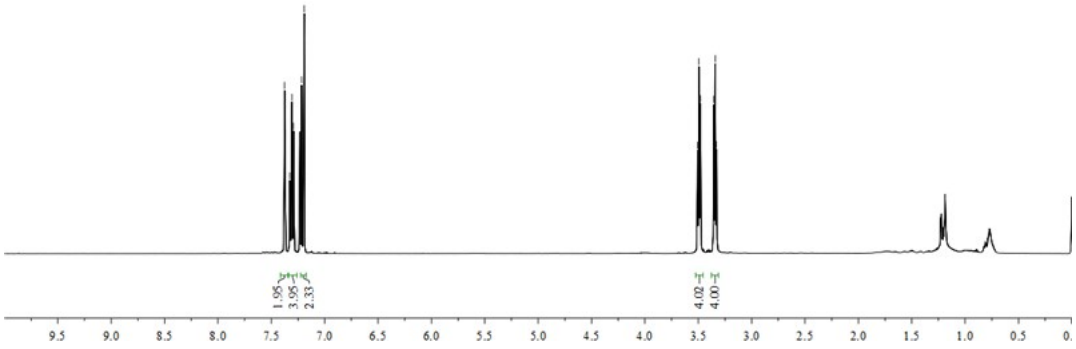

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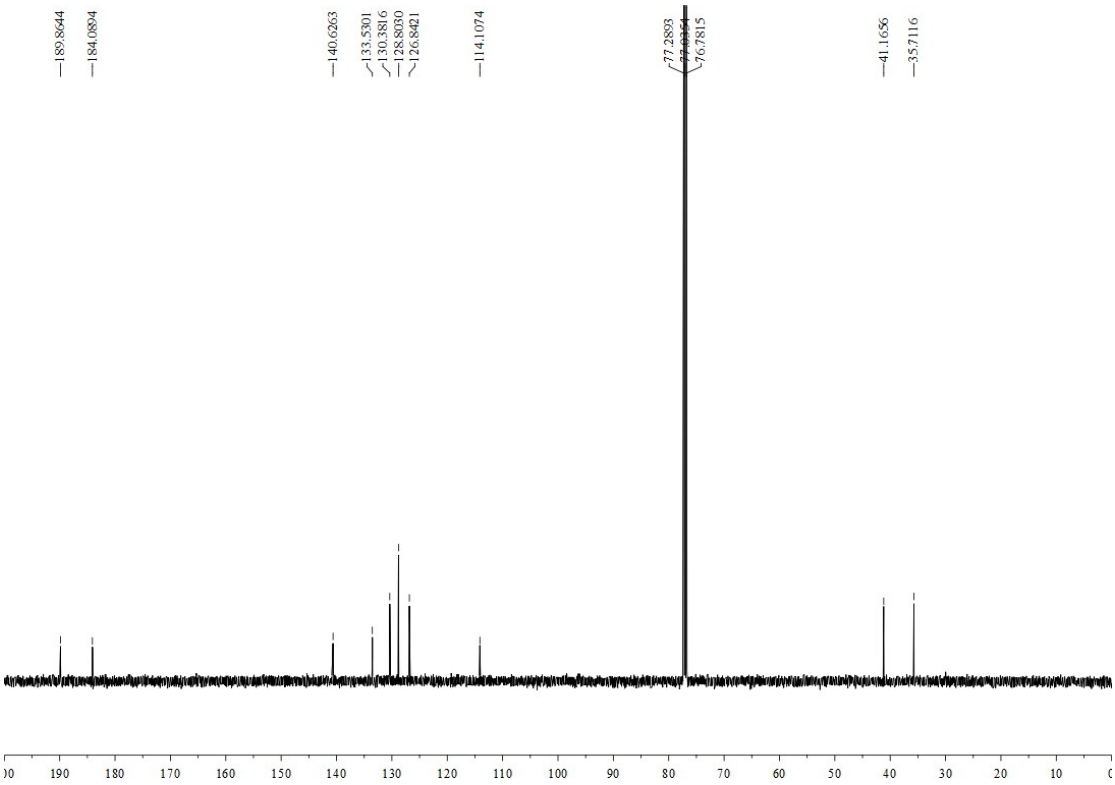

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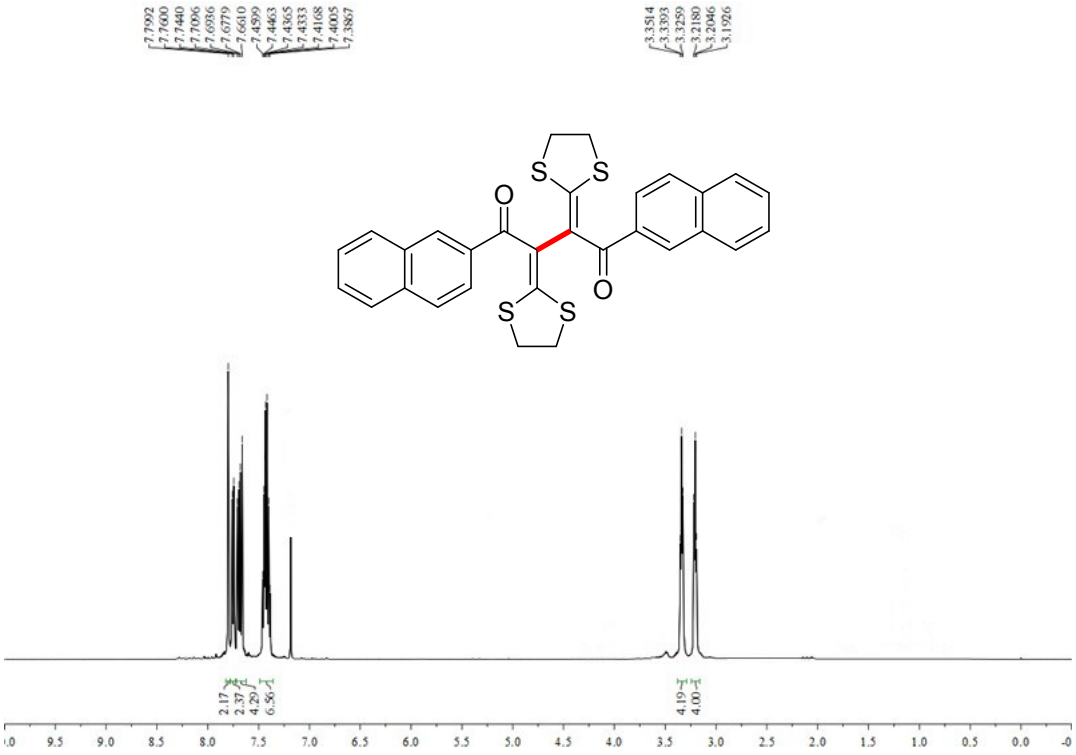

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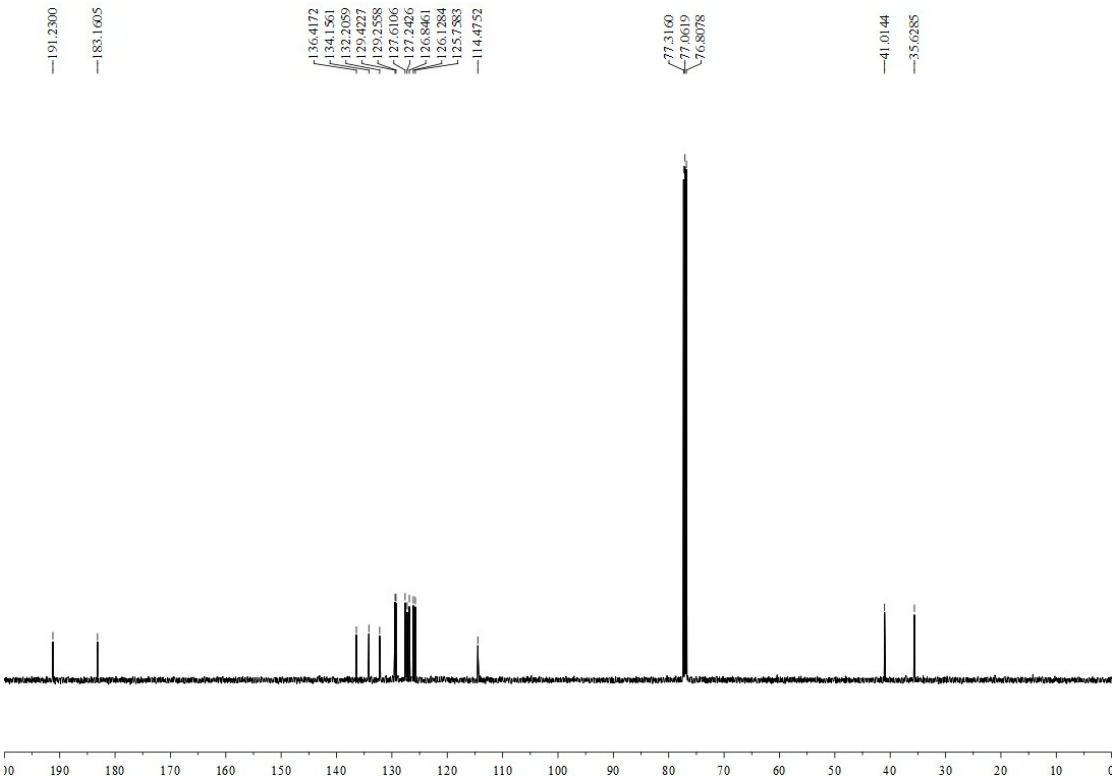

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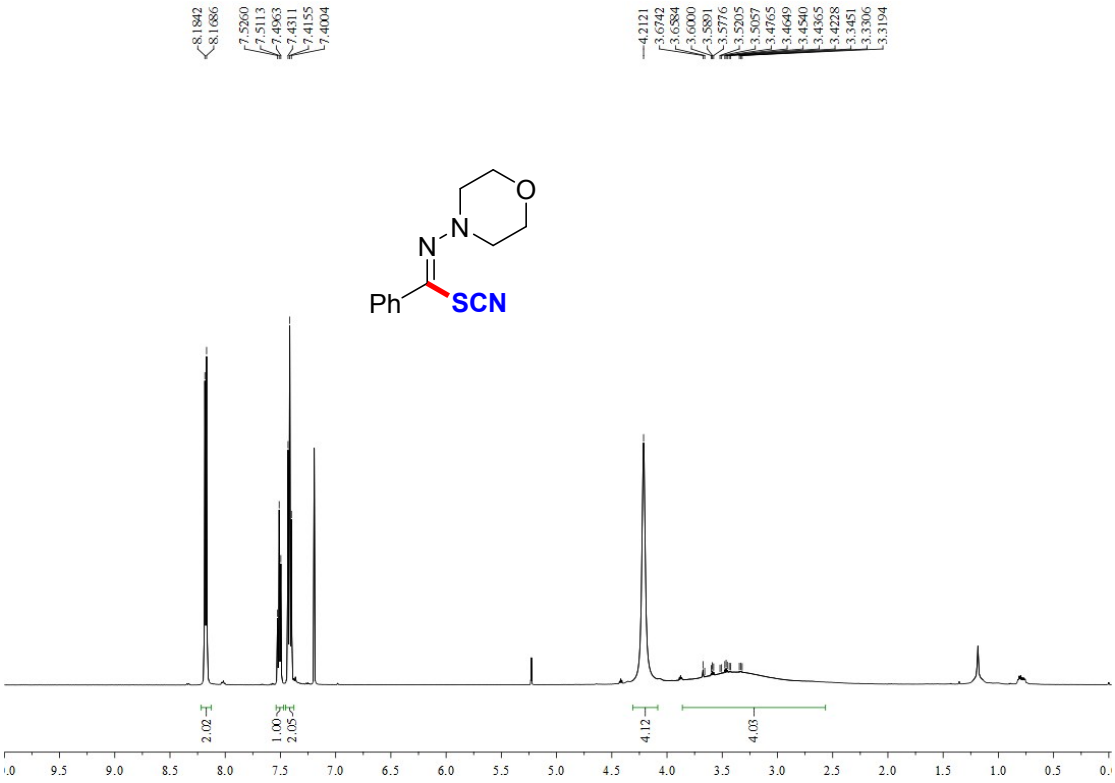

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